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GEOCHIMICA ET COSMOCHIMICA ACTA

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The geochemistry of some igneous rock series

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(Received 12 December, 1952)

ABSTRACT

This is the first of four papers concerning the distribution of some of the commoner trace elements with respect to the major elements in various igneous rock series. The present communication deals with certain calc-alkali igneous rock series, namely, the rocks of the Southern California batholith, the lavas of Lassen Peak, Crater Lake, the Lesser Antilles, the Medicine Lake Highlands and the East Central Sierra Nevada. These are compared with the Scottish Caledonian igneous rocks.

INTRODUCTION

The object of the present investigation is to study the behaviour of the trace elements with respect to the major constituents in some well known igneous rock series of calc-alkali, alkali, and tholeiitic character, to determine how their behaviour varies from series to series and from group to group, and to discover what light, if any, they throw on the origin of the three main branches of igneous rock evolution. It is proposed to publish three papers dealing respectively with the calc-alkali group, the alkali group and the tholeiitic group, and to summarize the results and conclusions in a fourth paper.

One of us (R.A.) has been responsible for taking the spectrograms and reading the results. The other (S.R.N.) has also read the results and is responsible for the writing of the paper.

A semi-quantitative spectrographic method has been used for the determination of the trace elements, the sample under investigation, mixed with an equal quantity of powdered carbon, being placed in a carbon electrode of the type devised by AHRENS and LIEBENBERG ((1946) type 5, Fig. 2, p. 136). This electrode is made the anode. A large quartz-glass Hilger spectrograph was used with a ten-stepped sector rotating in front of the slit. A standard average "igneous rock" was made up from pure constituents (well mixed, and the whole sintered at 900°C) to which known amounts of the trace elements were added. The number of steps in which a given line of an element was visible was then plotted against the logarithm of the concentration and a kind of working curve, normally a straight line through most of its range, was obtained.

When a line just appeared very faintly in the final step, this was taken as half a step, and it was found that results were normally reproducible to within $\pm$ half a step. In some cases, the line used for an element filled up all ten steps at quite a low concentration. Another, less sensitive, line of the same element was then used for the higher concentrations.

The unknown samples were arced, and the plates developed, under exactly the same conditions as the known standards and the number of steps in which a given line of an element was visible gave the concentration of that element in the unknown sample. In general, the method gives an accuracy of about $\pm$ 30% which was considered accurate enough for the particular purpose in view. All the results given for the trace elements were determined in this way with the exception of Ga, Tl and In. For these the volatile method described by AHRENS (1950) was used and the concentrations determined by visual comparison with known standards.

Most of the other elements were determined from lines within the range 2800–4600 Å, for

which Kodak B10 spectrographic plates were used. The arc gap was 10 mm with a current of 8 Amp and the sample was burned to completion. For Cs, Rb, Li, Ba and Sr the glass optical train was utilised, using Kodak 11N spectrographic plates and an arc gap of 14 mm with a current of 8 Amp. The main advantage of using the glass instead of the quartz optical train was that the Cs line 8521 Å was much more sensitive and Cs could be determined down to about 15 ppm. Kodak 0-0 spectrographic plates were used for the determination of Ga, Tl and In, with an arc gap of 10 mm and a current of 2.5 Amp, the burn being stopped after 30 seconds.

In an investigation of this kind it is important that the results should be comparable in all the rock series investigated. To make sure of this, random samples of other series were taken at the same time as those of any particular series and the results checked with those previously found for the samples in question. For many samples duplicate burns were made and, in every case, the concentrations of the elements were determined independently by both of us. A few determinations of boron were made, using copper electrodes, an arc gap of 5 mm and a current of 2.5 Amp.

List of Lines Used

B	2497.73, 2496.78	Ag	3382.89
Pb	2833.07	In	4101.77
Sn	2840.0	Tl	3775.72
Be	3130.4, 3131.1	Ga	4172.06
Mo	3170.3		
V	3189.4		
Y	3327.88	Sr	4607.33
Ni	3414.77	Ba	4934.09
	3452.89 (> 400 ppm)	Li	6707.84
Zr	3438.23	Rb	7800.23
Co	3453.5	Cs	8521.1
Sc	4246.83		
Cr	4254.35		
	4339.45 (> 400 ppm)		
La	4333.73		

1. CALC-ALKALI IGNEOUS ROCK SERIES

The following igneous rock series of calc-alkali type have been investigated: the Southern California batholith; Lassen Peak; Medicine Lake; East Central Sierra Nevada; Crater Lake; Lesser Antilles; while we have for comparison the Scottish Caledonian series already published.

(1) *The Southern California batholith*

The various intrusions which make up the great South California batholith have been described in detail by LARSEN (1948). A variation diagram showing the relationship between Mg, (Fe²⁺ + Fe³⁺) and (Na + K) and between Ca, Na and K is given in Fig. 1. It can be seen that the bulk of the rocks fall on a smooth curve in each case until a certain position at the basic end is reached. Beyond this, there is more or less random scattering. The basic end of the smooth curves is believed to represent the *parental magma*, and the scattered points beyond this, all of which represent early phases of the batholith, are interpreted as *accumulative rocks*. The average composition of the parental magma will be found in Table 8, column 5 and Table 9, column 4.

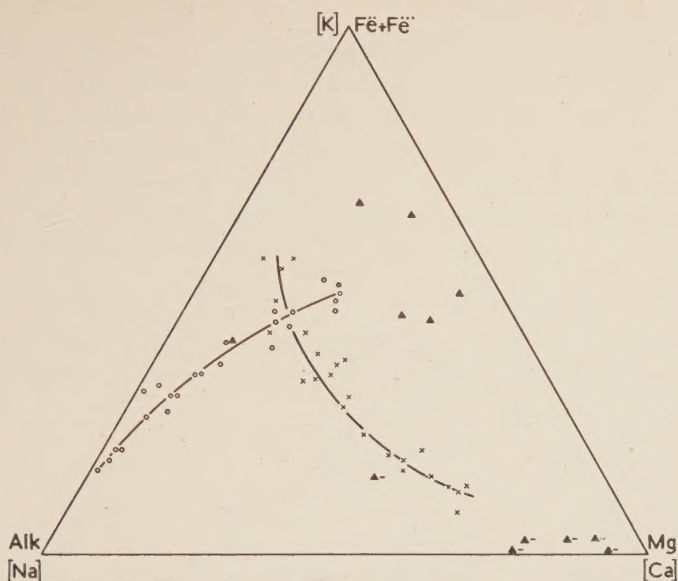


Fig. 1. Variation diagram of the rocks of the Southern California batholith. Small circles and the full curve refer to variations in $(\text{Fe}'' + \text{Fe}''')$, Mg, and $(\text{Na} + \text{K})$; crosses and the dashed curve refer to variation in Ca, Na, and K; triangles represent accumulative rocks.

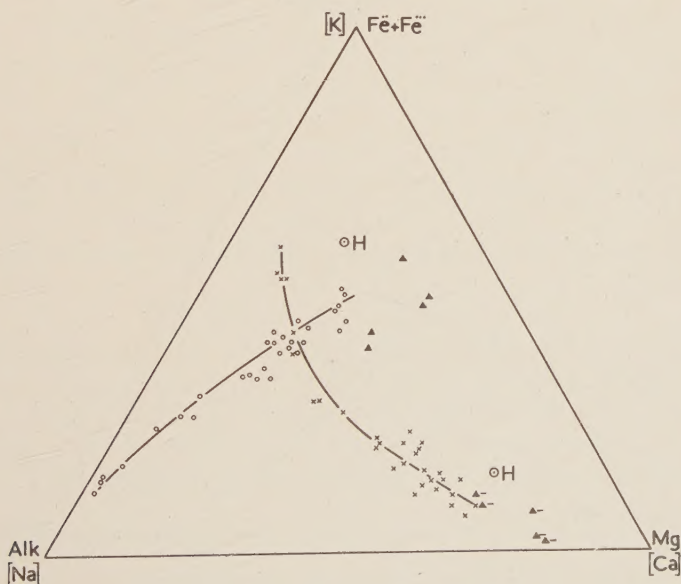


Fig. 2. Variation diagram of the rocks of the Lassen Peak area. H refers to Harkness basalt.

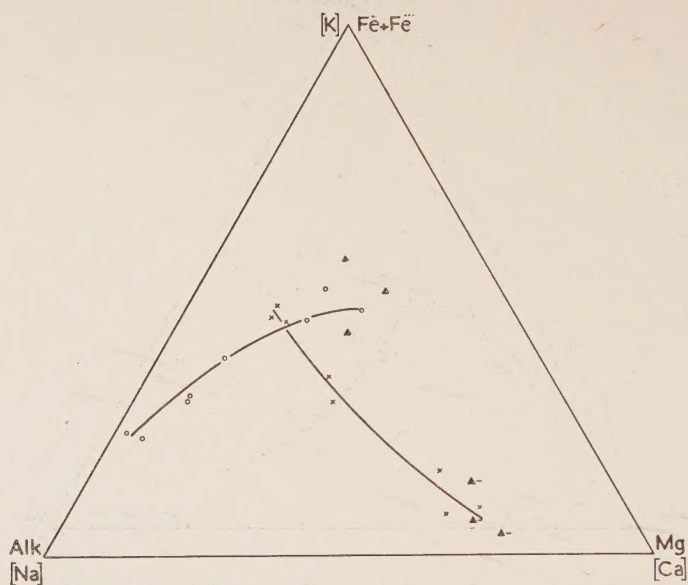


Fig. 3. Variation diagram of the recent rocks of the Medicine Lake Highlands.

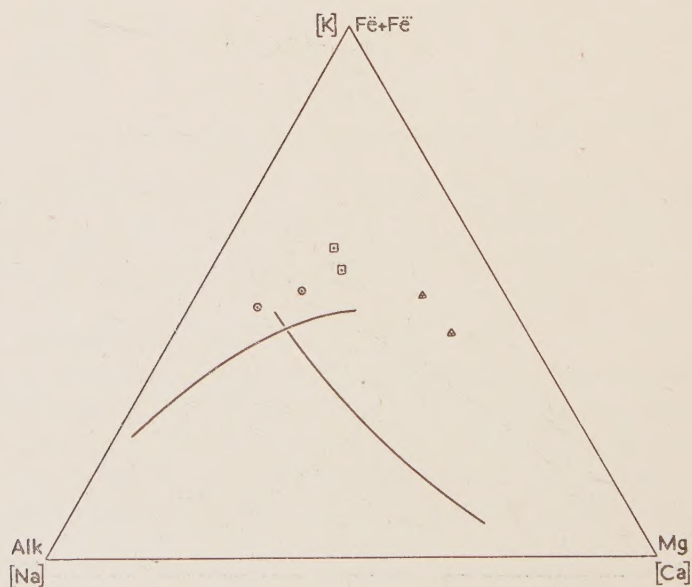


Fig. 4. As Fig. 3, but with the earlier Warner basalts, Lake basalts and platy andesites of the Shield volcano added. Warner basalts represented by triangles, Lake basalts by squares, platy andesites by dots surrounded by circles.

(b) *Lassen Peak area*

The volcanic rocks of the Lassen Peak area have been studied most recently by WILLIAMS (1932), and numerous chemical analyses are available. The variation diagram is shown in Fig. 2. Here again, there are the same smooth curves of variation and the same scattering of points at the basic end of the curves. Moreover, both the curves of variation are similar in form to those of the Southern California batholith. The composition of the supposed parental magma is given in Table 8, column 4, and Table 9, column 3.

(c) *Medicine Lake Highlands*

The lavas of the Medicine Lake Highlands have been discussed by ANDERSON (1941). Only certain of these lavas concern us here, namely, the Modoc basalts,

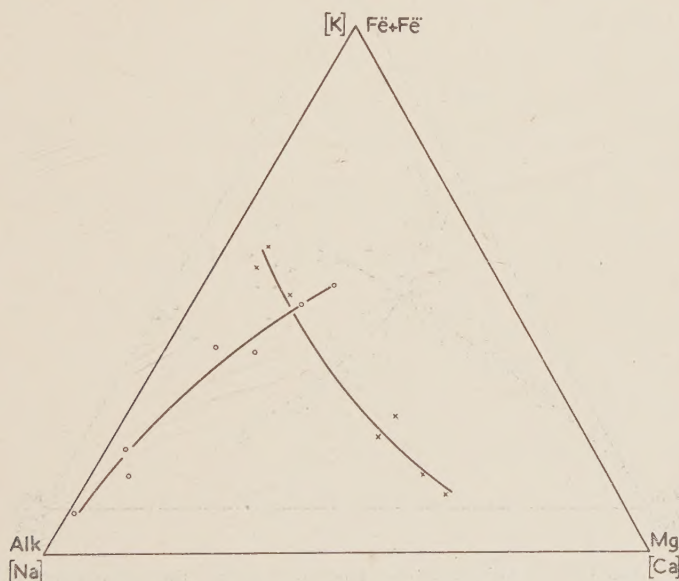


Fig. 5. Variation diagram of the calc-alkali series of rocks from East Central Sierra Nevada.

the basalt inclusion found in dacite, the dacites and the rhyolite-obsidians of Glass Mountain. Those belong to a well-marked series (see Fig. 3) to which the earlier Warner basalts, Lake basalts and platy andesites of the Shield volcano do not belong (Fig. 4). We believe the parental magma to have a composition approximating to that given in Table 8, column 2, and Table 9, column 2.

(d) *East Central Sierra Nevada*

The lavas of the East Central Sierra Nevada have been investigated by HALSEY (1951), CURTIS (1952) and SLEMMONS (1952) who have kindly allowed us to make use of their unpublished chemical analyses. Two series are present—a normal

calc-alkali series ranging from pyroxene andesite to rhyolite, and a somewhat later latite series. The variation diagram for the former series is shown in Fig. 5. The composition of the supposed parental magma is given in Table 8, column 6 and Table 9, column 5.

(e) *Scottish Caledonian and Old Red Sandstone igneous rocks*

These have already been dealt with elsewhere by NOCKOLDS and MITCHELL (1948) and are inserted here for comparison. The variation diagram, with the accumulative rocks omitted for the Ca-Na-K portion of the diagram, is shown in Fig. 6 and the composition of the supposed parental magma is given in Table 8, column 1 and Table 9, column 1.

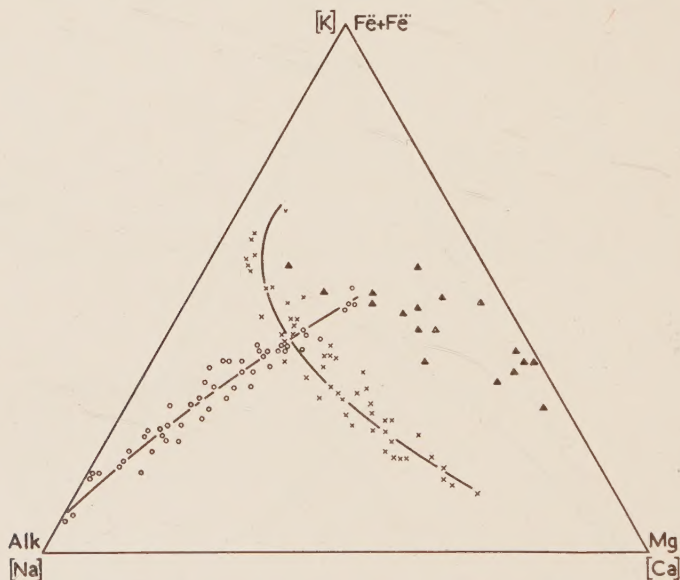


Fig. 6. Variation diagram of the Scottish Caledonian rocks, for comparison with the others.

It is evident from a study of the variation diagrams that these five examples of calc-alkali rock series are all very similar, the curves of variation having the same form in each case, in spite of the fact that some series are volcanic, while the Scottish Caledonian series has volcanic, hypabyssal, and plutonic representatives, and the Southern California batholith series is largely plutonic. It seems most unlikely, that a group of rock series showing such similar variation should have formed in quite different ways and it is concluded that *all* these series are magmatic and have crystallized from a melt. This being so, the smooth curves of variation are believed to represent, in each case, the liquid line of descent of the parental magma, and the rocks which we have already termed accumulative represent original magmatic liquid together with a varying amount of accumulated solid crystals.

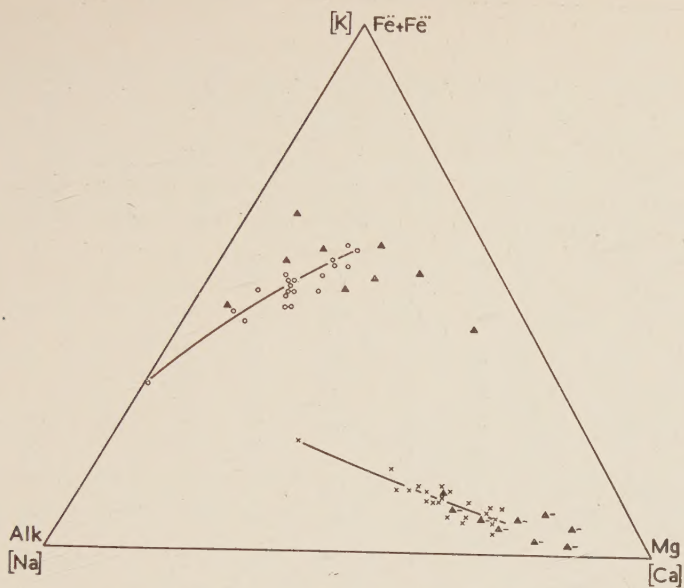


Fig. 7. Variation diagram of the rocks of the Lesser Antilles.

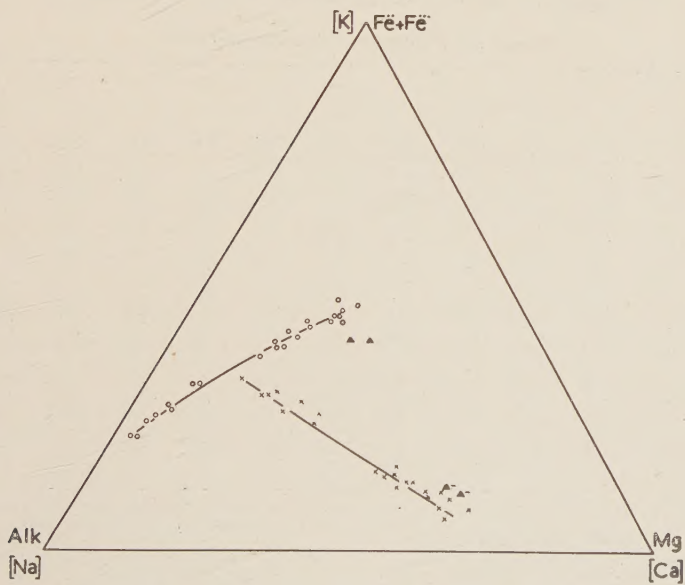


Fig. 8. Variation diagram of the rocks of Crater Lake and Mount Shasta.

Table 1. *Rocks of the Southern California Batholith†*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Si ⁺⁴	201·10 ³	228·10 ³	214·10 ³	222·10 ³	244·10 ³	266·10 ³	260·10 ³	275·10 ³	278·10 ³	299·10 ³	294·10 ³	284·10 ³	326·10 ³	326·10 ³	321·10 ³
Al ⁺³	132·10 ³	106·10 ³	83·10 ³	97·10 ³	111·10 ³	87·10 ³	95·10 ³	92·10 ³	95·10 ³	82·10 ³	89·10 ³	107·10 ³	77·10 ³	75·10 ³	83·10 ³
Ti ⁺⁴	12·10 ²	48·10 ²	306·10 ²	96·10 ²	18·10 ²	78·10 ²	54·10 ²	42·10 ²	54·10 ²	36·10 ²	42·10 ²	42·10 ²	30·10 ²	30·10 ²	24·10 ²
Fe ⁺³	15·10 ³	11·10 ³	13·10 ³	43·10 ³	2·10 ³	13·10 ³	15·10 ³	10·10 ³	11·10 ³	11·10 ³	6·10 ³	2·10 ³	14·10 ³	9·10 ³	13·10 ³
Mg ⁺²	56·10 ³	46·10 ³	43·10 ³	30·10 ³	41·10 ³	30·10 ³	26·10 ³	27·10 ³	19·10 ³	19·10 ³	14·10 ³	10·10 ³	8·10 ³	10·10 ³	8·10 ³
Fe ⁺²	48·10 ³	40·10 ³	85·10 ³	61·10 ³	51·10 ³	46·10 ³	52·10 ³	40·10 ³	39·10 ³	33·10 ³	42·10 ³	35·10 ³	18·10 ³	23·10 ³	16·10 ³
Na ⁺¹	6·10 ³	14·10 ³	7·10 ³	21·10 ³	18·10 ³	22·10 ³	24·10 ³	22·10 ³	25·10 ³	22·10 ³	26·10 ³	33·10 ³	25·10 ³	27·10 ³	26·10 ³
Ca ⁺²	94·10 ³	98·10 ³	85·10 ³	75·10 ³	72·10 ³	57·10 ³	54·10 ³	54·10 ³	47·10 ³	41·10 ³	41·10 ³	40·10 ³	29·10 ³	25·10 ³	26·10 ³
K ⁺¹	8·10 ²	25·10 ²	33·10 ²	11·10 ²	25·10 ²	116·10 ²	116·10 ²	100·10 ²	133·10 ²	158·10 ²	125·10 ²	133·10 ²	158·10 ²	20·10 ³	23·10 ³
B ⁺³	*	—	*	*	*	30	10	20	10	15	10	10	—	50	*
Ga ⁺³	45	25	40	40	35	30	25	25	40	25	30	30	20	20	20
Cr ⁺³	200	350	20	5	50	75	45	70	20	50	30	5	3	30	5
V ⁺³	80	150	550	300	200	150	150	110	120	110	100	75	50	100	60
Mo ⁺⁴	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Li ⁺¹	5	10	10	5	5	25	25	20	40	30	45	50	20	25	30
Ni ⁺²	30	20	*	*	30	30	10	30	5	30	5	*	*	15	*
Co ⁺²	55	25	25	30	40	20	20	20	15	20	10	5	5	15	*
Sc ⁺³	*	50	50	35	35	25	30	30	20	25	20	*	*	15	*
Zr ⁺⁴	10	40	30	15	15	75	75	100	75	150	100	100	150	300	200
Y ⁺³	*	15	10	*	*	20	20	15	15	30	20	25	20	40	20
La ⁺³	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Sr ⁺²	500	600	250	1000	550	275	250	275	200	250	250	300	250	250	275
Pb ⁺²	*	*	*	*	*	10	*	*	*	10	10	10	15	10	10
Ba ⁺²	5	70	20	10	20	300	250	250	700	400	700	400	850	650	900
Cs ⁺¹	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Rb ⁺¹	*	10	*	*	*	100	100	100	200	100	125	125	50	100	175
Tl ⁺¹	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Position	-8·2	-6·5	-5·3	-3·0	-2·9	+1·3	+1·9	+2·1	+4·0	+5·6	+5·6	+5·8	+8·8	+9·4	+9·6
{Fe	53	53	70	78	56	66	72	65	72	70	77	79	80	76	78
{Mg	47	47	30	22	44	34	28	35	28	30	23	21	20	24	22
{Fe	50	45	65	67	46	48	52	46	46	43	48	40	40	36	34
{Mg	44	41	28	19	36	24	20	25	18	19	14	11	10	11	9
{Alk	6	14	7	14	18	28	28	29	36	38	38	49	50	53	57

† Values for the elements in this and following tables are given in ppm.

Table 1a. *Southern California Batholith*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ga × 1000/Al	0·34	0·24	0·48	0·41	0·32	0·35	0·25	0·27	0·42	0·30	0·34	0·28	0·26	0·27	0·24
Cr × 1000/Mg	3·6	7·6	0·5	0·2	1·2	2·5	1·7	2·6	1·1	2·6	2·1	0·5	0·4	3·0	0·6
V × 1000/Mg	1·4	3·3	13	10	4·9	5·0	5·8	4·1	6·3	5·8	7·1	7·5	6·3	10	7·5
Li × 1000/Mg	0·1	0·2	0·2	0·2	0·1	0·8	1·0	0·7	2·1	1·6	3·2	5·0	2·5	2·5	3·7
Ni × 1000/Mg	0·5	0·4	*	*	0·7	1·0	0·4	1·1	0·3	1·6	0·4	*	*	1·5	*
Ca × 1000/Mg	1·0	0·5	0·6	1·0	1·0	0·7	0·8	0·7	0·8	1·1	0·7	0·5	0·6	1·5	*
Fe/Mg	1·1	1·1	2·3	3·5	1·3	2·0	2·6	1·9	2·6	2·3	3·4	3·7	4·0	3·2	3·6
Sc × 1000/Mg	*	1·1	1·2	1·2	0·9	0·8	1·2	1·1	1·1	1·3	1·4	*	*	1·5	*
Cr × 1000/Fe	3·2	6·9	0·2	0·05	0·9	1·3	0·7	1·4	0·4	1·1	0·6	0·1	0·1	0·9	0·2
V × 1000/Fe	1·3	2·9	5·6	2·9	3·8	2·5	2·2	2·2	2·4	2·5	2·1	2·0	1·6	3·1	2·1
Co × 1000/Fe	0·9	0·5	0·3	0·3	0·8	0·3	0·3	0·4	0·3	0·5	0·2	0·1	0·2	0·5	*
Sc × 1000/Fe	*	1·0	0·5	0·3	0·7	0·4	0·4	0·6	0·4	0·6	0·4	*	*	0·5	*
Y × 1000/Ca	*	0·15	0·1	*	*	0·35	0·4	0·3	0·3	0·7	0·5	0·6	0·7	1·6	0·8
Sr × 100/Ca	0·5	0·6	0·3	1·3	0·8	0·5	0·5	0·5	0·4	0·6	0·6	0·75	0·9	1·0	1·1
Sr × 100/Ca + K	0·5	0·6	0·3	1·3	0·7	0·4	0·4	0·4	0·3	0·4	0·5	0·6	0·6	0·6	0·6
Ba × 100/K	0·6	2·8	0·6	0·9	0·8	2·6	2·2	2·5	5·3	2·5	5·6	3·0	5·3	3·3	3·9
Rb × 100/K	*	0·4	*	*	*	0·9	0·9	1·0	1·5	0·6	1·0	0·9	0·3	0·5	0·8

Early Accumulative Rocks

1. Olivine norite (with hornblende). LARSEN (1948), Anal. 1, p. 50.
2. Noritic hornblende gabbro. LARSEN (1948), Anal. 4, p. 50.
3. Calcic hornblende gabbro (rich in iron ore). LARSEN (1948), Anal. 2, p. 50.
4. Norite (rich in iron ore). LARSEN (1948), Anal. 3, p. 50.
5. Typical norite. LARSEN (1948), Anal. 5, p. 50.

Rocks on Liquid Line of Descent

6. Coarse quartz-biotite norite. LARSEN (1948), Anal. 9, p. 50.
7. Bonsall tonalite. LARSEN (1948), Anal. 2, p. 66.

8. Quartz-biotite-hornblende gabbro. LARSEN (1948), Anal. 9.
9. Lakeview Mountain tonalite. LARSEN (1948), Anal. 7, p. 56.
10. Green Valley tonalite. LARSEN (1948), Anal. 2, p. 56.
11. Bonsall tonalite. LARSEN (1948), Anal. 3, p. 66.
12. La Sierra tonalite (enriched in plagioclase). LARSEN (1948), Anal. p. 73 (has high Al and Na).
13. Domenigoni Valley granodiorite. LARSEN (1948), Anal. 1.
14. Green Valley tonalite. LARSEN (1948), Anal. 1, p. 56.
15. Porphyritic granodiorite. LARSEN (1948), Anal. p. 93.
16. Light-coloured dike. LARSEN (1948), Anal. p. 102.
17. Granodiorite west of Lakeview. LARSEN (1948), Anal. 1.
18. Quartz latite porphyry. LARSEN (1948), Anal. p. 105.

The geochemistry of some igneous rock series

Table 1. Rocks of the Southern California Batholith† (cont.)

18	19	20	21	22	23	24	25	26	27	28	29	30	Sensi- tivity, ppm	Ionic Radius]	
333-10 ³	333-10 ³	341-10 ³	341-10 ³	351-10 ³	345-10 ³	360-10 ³	349-10 ³	353-10 ³	329-10 ³	344-10 ³	351-10 ³	340-10 ³	—	0-42	Si ⁺⁴
79-10 ³	77-10 ³	75-10 ³	70-10 ³	73-10 ³	74-10 ³	64-10 ³	70-10 ³	68-10 ³	89-10 ³	77-10 ³	74-10 ³	75-10 ³	—	0-51	Al ⁺³
18-10 ²	36-10 ²	18-10 ²	30-10 ²	12-10 ²	12-10 ²	12-10 ²	12-10 ²	6-10 ²	18-10 ²	18-10 ²	12-10 ²	18-10 ²	—	0-68	Ti ⁻⁴
6-10 ³	10-10 ³	5-10 ³	9-10 ³	3-10 ³	4-10 ³	4-10 ³	10-10 ³	6-10 ³	9-10 ³	7-10 ³	6-10 ³	8-10 ³	—	0-64	Fe ⁺³
5-10 ³	2-10 ³	6-10 ²	4-10 ³	1-10 ³	2-10 ³	2-10 ³	2-10 ³	1-10 ³	4-10 ³	2-10 ³	1-10 ³	6-10 ³	—	0-66	Mg ⁺²
17-10 ³	15-10 ³	19-10 ³	12-10 ³	10-10 ³	12-10 ³	9-10 ³	7-10 ³	7-10 ³	10-10 ³	13-10 ³	9-10 ³	11-10 ³	—	0-74	Fe ⁻²
26-10 ³	25-10 ³	29-10 ³	27-10 ³	28-10 ³	28-10 ³	23-10 ³	22-10 ³	26-10 ³	30-10 ³	29-10 ³	30-10 ³	20-10 ³	—	0-97	Na ⁺¹
21-10 ³	22-10 ³	18-10 ³	16-10 ³	11-10 ³	10-10 ³	8-10 ³	9-10 ³	6-10 ³	26-10 ³	20-10 ³	16-10 ³	16-10 ³	—	0-99	Ca ⁺²
24-10 ³	26-10 ³	23-10 ³	31-10 ³	28-10 ³	36-10 ³	36-10 ³	41-10 ³	41-10 ³	11-10 ³	15-10 ³	17-10 ³	35-10 ³	—	1-33	K ⁺¹
—	22	*	15	22	*	22	*	*	2	22	*	5	2	0-23	B ⁺³
20	20	20	15	15	15	15	15	20	25	25	25	15	2	0-62	Ga ⁺³
2	15	*	2	*	*	*	*	*	1	3	*	2	2	0-63	Cr ⁺³
40	75	40	30	10	15	5	*	*	30	50	5	30	5	0-74	V ⁺³
*	*	*	*	*	*	*	4	*	*	*	*	*	2	0-70	Mo ⁺⁴
20	15	50	50	30	50	50	10	50	40	10	60	100	1	0-68	Li ⁺¹
*	5	*	*	*	*	*	*	*	*	3	*	*	3	0-69	Ni ⁺²
*	10	*	*	*	*	*	*	*	*	5	*	*	3	0-72	Co ⁺²
*	*	*	*	*	*	*	*	*	*	*	*	*	10	0-81	Sc ⁺³
200	150	150	150	80	100	70	250	80	200	200	100	120	10	0-79	Zr ⁺⁴
35	30	40	40	30	30	40	45	25	*	45	20	30	10	0-92	Y ⁺³
*	*	50	*	50	50	50	75	100	75	*	*	*	40	1-14	La ⁺³
300	250	175	150	80	125	80	75	30	900	200	200	175	2	1-12	Sr ⁺²
10	210	10	15	20	15	20	30	20	10	15	20	15	10	1-20	Pb ⁺²
800	700	800	900	1000	1250	1000	1250	1250	800	850	700	1000	5	1-34	Ba ⁺²
*	*	*	*	*	215	*	*	15	215	*	*	*	15	1-67	Cs ⁺¹
100	250	200	300	100	250	300	400	350	50	50	50	250	10	1-47	Rb ⁺¹
*	*	*	22	*	*	*	*	22	*	*	22	*	2	1-47	Tl ⁺¹
+10-9	+11-3	+11-8	+12-5	+13-3	+13-9	+14-6	+14-6	+15-2	+9-1	+10-8	+11-7	+12-6			
81	91	98	85	91	90	88	87	91	82	92	92	76			
19	9	2	15	9	10	12	13	9	18	8	8	24			
30	32	31	26	16	20	18	20	18	30	30	23	24			
7	3	1	4	1	2	2	3	2	7	3	2	7			
63	65	68	70	83	78	80	77	80	63	67	75	69			

† Values for the elements in this and following tables are given in ppm.

Table 1a. Southern California Batholith (cont.)

18	19	20	21	22	23	24	25	26	27	28	29	30	
0-25	0-26	0-27	0-21	0-21	0-20	0-23	0-21	0-29	0-28	0-32	0-34	0-20	Ga × 1000/Al
0-4	7-5	*	0-5	*	*	*	*	*	0-25	1-5	*	0-3	Cr × 1000/Mg
8-0	37	67	7-5	10	7-5	2-5	*	*	7-5	25	5	5	V × 1000/Mg
4-0	7-5	83	12	30	25	25	5	50	10	5	60	17	Li × 1000/Mg
*	2-5	*	*	*	*	*	*	*	*	1-5	*	*	Ni × 1000/Mg
*	5-0	*	*	*	*	*	*	*	*	2-5	*	*	Co × 1000/Mg
4-6	12-5	40	5-2	13	8-0	6-5	8-5	13	4-8	10	15	3-2	Fe/Mg
*	*	*	*	*	*	*	*	*	*	*	*	*	Sc × 1000/Mg
0-1	0-6	*	0-1	*	*	*	*	*	0-05	0-15	*	0-1	Cr × 1000/Fe
1-7	3-0	1-7	1-4	0-8	0-9	0-4	*	*	1-6	2-5	0-3	1-6	V × 1000/Fe
*	0-4	*	*	*	*	*	*	*	*	0-25	*	*	Co × 1000/Fe
*	*	*	*	*	*	*	*	*	*	*	*	*	Sc × 1000/Fe
1-7	1-4	2-2	2-5	2-7	3-0	5-0	5-0	4-1	*	2-2	1-3	1-9	Y × 1000/Ca
1-4	1-1	1-0	0-9	0-7	1-2	1-0	0-8	0-5	3-5	1-0	1-3	1-1	Sr × 100/Ca
0-7	0-5	0-4	0-3	0-2	0-3	0-2	0-1	0-1	2-4	0-6	0-6	0-3	Sr × 100/Ca + K
3-3	2-7	3-5	2-9	3-6	3-5	2-8	3-0	3-0	7-3	5-7	4-1	2-9	Ba × 100/K
0-4	1-0	0-9	1-0	0-4	0-7	0-8	1-0	0-9	0-5	0-3	0-3	0-7	Rb × 100/K

nsal tonalite. LARSEN (1948), Anal., 5, p. 66.
Woodson Mountain granodiorite. LARSEN (1948), Anal. 1, p. 80.
Hole granodiorite. LARSEN (1948), Anal., p. 91.
Woodson Mountain granodiorite. LARSEN (1948), Anal. 4, p. 80.
Large grained granite of Rubidoux Mountain. LARSEN (1948),
100.
blar leucogranite. LARSEN (1948), Anal., p. 98.
cropegmatite granite (altered). LARSEN (1948), Anal., p. 99
Li and presence of Mo).
Large grained granite of Rubidoux Mountain. LARSEN (1948),
100.

Rocks Slightly off the Liquid Line of Descent

27. Tonalite near Aguanga. LARSEN (1948), Anal. 8, p. 66 (noted by LARSEN, p. 141, as abnormal).

28. Escondido Creek leucogranodiorite. LARSEN (1948), Anal., p. 89 (said to be moderately altered with development of much epidote and some chlorite).

29. Lake Wolford leucogranodiorite. LARSEN (1948), Anal., p. 85 (stated by LARSEN, p. 141, to be not typical of this intrusion).

30. Woodson Mountain granodiorite. LARSEN (1948), Anal. 2, p. 80.

Table 2. *Rocks of Lassen Peak*

	<i>H</i>	1	2	3	4	5	6	7	8	9
Si ⁺⁴	228·10 ³	225·10 ³	271·10 ³	257·10 ³	278·10 ³	291·10 ³	292·10 ³	296·10 ³	333·10 ³	326·10 ³
Al ⁺³	72·10 ³	98·10 ³	89·10 ³	91·10 ³	91·10 ³	87·10 ³	89·10 ³	89·10 ³	76·10 ³	82·10 ³
Ti ⁺⁴	25·10 ³	40·10 ²	40·10 ²	80·10 ²	50·10 ²	40·10 ²	40·10 ²	40·10 ²	20·10 ²	(20·10 ²)
Fe ⁺³	41·10 ³	15·10 ³	6·10 ³	11·10 ³	16·10 ³	8·10 ³	14·10 ³	11·10 ³	9·10 ³	23·10 ³
Mg ⁺²	32·10 ³	55·10 ³	37·10 ³	33·10 ³	22·10 ³	20·10 ³	20·10 ³	17·10 ³	5·10 ³	10·10 ³
Fe ⁺²	56·10 ³	57·10 ³	38·10 ³	45·10 ³	30·10 ³	31·10 ³	19·10 ³	22·10 ³	10·10 ³	—
Na ⁺¹	20·10 ³	17·10 ³	22·10 ³	27·10 ³	27·10 ³	25·10 ³	26·10 ³	27·10 ³	32·10 ³	29·10 ³
Ca ⁺²	69·10 ³	80·10 ³	59·10 ³	56·10 ³	51·10 ³	45·10 ³	43·10 ³	41·10 ³	23·10 ³	15·10 ³
K ⁺¹	16·10 ³	17·10 ²	10·10 ³	15·10 ³	13·10 ³	17·10 ³	21·10 ³	18·10 ³	23·10 ³	27·10 ³
B ⁺³	5	2	*	?2	2	—	—	—	5	10
Ga ⁺³	15	25	25	20	20	20	20	20	20	20
Cr ⁺³	20	400	200	150	50	80	50	30	5	10
V ⁺³	170	300	200	100	120	100	65	50	50	50
Li ⁺¹	20	15	25	40	45	60	50	40	50	50
Ni ⁺²	25	175	75	50	25	25	30	20	5	*
Co ⁺²	25	65	30	20	20	15	10	10	10	*
Se ⁺³	?10	50	25	15	20	20	15	15	*	*
Zr ⁺⁴	200	60	80	100	100	80	125	100	100	120
Y ⁺³	20	40	15	20	20	25	25	15	20	10
La ⁺³	*	*	*	*	*	*	*	*	*	*
Sr ⁺²	650	1000	1000	1000	1000	1000	1250	1250	1500	1000
Pb ⁺²	*	*	*	*	*	*	?10	*	10	25
Ba ⁺²	450	70	400	550	700	1000	1000	800	500	1000
Rb ⁺¹	100	*	40	100	80	100	100	100	50	200
Cs ⁺¹	—	*	—	—	—	—	—	—	—	*
Position	—0·9	—5·8	+0·4	+1·2	+3·3	+4·9	+5·5	+5·9	+10·6	+11·1
{ Fe	75	57	54	62	68	66	62	66	79	70
{ Mg	25	43	46	38	32	34	38	34	21	30
{ Fe	59	49	39	46	43	39	33	35	24	26
{ Mg	19	38	33	24	21	20	20	18	6	11
{ Alk	22	13	28	30	36	41	47	47	70	63

(f) *Lesser Antilles*

A considerable body of data is available on the lavas of the Lesser Antilles through the publications of LACROIX (1924) and of A. G. MCGREGOR (1938). The variation diagram is given in Fig. 7 and, while the curve of variation for Mg, Fe and Alkalies is not unlike those of the previous series, the curve for Ca, Na and K takes a different course. It should be mentioned that LACROIX describes a number of lavas which have been contaminated. Some of these show grains of quartz surrounded by a corona of pyroxene, others have been affected by argillaceous sediment which may lead to the development of cordierite. In both cases, these lavas lie off the curves of variation and they have been omitted from the figure so as not to cause confusion with the accumulative types. The composition of the supposed parental magma will be found in Table 8, column 10, and Table 9, column 8.

Table 2a. Lassen Peak

	H	1	2	3	4	5	6	7	8	9
Ga $\times$ 1000/Al	0.21	0.26	0.28	0.22	0.22	0.23	0.22	0.22	0.26	0.24
Cr $\times$ 1000/Mg	0.6	7.3	5.4	4.5	2.3	4.0	2.5	1.8	1.0	1.0
V $\times$ 1000/Mg	5.3	5.5	5.4	3.0	5.5	5.0	3.2	2.9	10.0	5.0
Li $\times$ 1000/Mg	0.6	0.3	0.7	1.2	2.0	3.0	2.5	2.4	10.0	5.0
Ni $\times$ 1000/Mg	0.8	3.2	2.0	1.5	1.1	1.2	1.5	1.2	1.4	*
Co $\times$ 1000/Mg	0.8	1.2	0.8	0.6	0.9	0.7	0.5	0.6	2.0	*
Fe/Mg	3.0	1.3	1.2	1.7	2.1	2.0	1.7	1.9	3.8	2.3
Sc $\times$ 1000/Mg	70.3	0.9	0.7	0.5	0.9	1.0	0.8	0.9	*	*
Cr $\times$ 1000/Fe	0.2	5.6	4.5	2.7	1.1	2.1	1.5	0.9	0.3	0.4
V $\times$ 1000/Fe	1.8	4.2	4.5	1.8	2.6	2.6	2.0	1.5	2.6	2.2
Co $\times$ 1000/Fe	0.3	0.9	0.7	0.4	0.4	0.4	0.3	0.3	0.5	*
Sc $\times$ 1000/Fe	70.1	0.7	0.6	0.3	0.4	0.5	0.5	0.5	*	*
Y $\times$ 1000/Ca	0.3	0.5	0.3	0.4	0.4	0.6	0.6	0.4	0.9	0.7
Sr $\times$ 100/Ca	0.9	1.3	1.7	1.8	2.0	2.2	2.9	3.0	6.5	6.6
Sr $\times$ 100/Ca + K	0.8	1.0	1.4	1.4	1.6	1.6	2.0	2.1	3.3	2.4
Ba $\times$ 100/K	2.8	0.4	4.0	3.7	5.3	5.9	4.8	4.4	2.2	3.7
Rb $\times$ 100/K	0.6	*	0.4	0.7	0.6	0.6	0.5	0.6	0.2	0.7

H. Harkness basalt. WILLIAMS (1932), Anal. 11, p. 280, (this rock has an abnormal composition with respect to both its major and trace elements and does not appear to belong to the Lassen Peak series).

1. Basalt, rather rich in olivine (accumulative), 1 mile S.E. of Paynes Creek. CLARKE (1915), Anal. L, p. 175.

2. Augite andesite, Hat Creek. WILLIAMS (1932), Anal. 15, p. 290.

3. Pyroxene basalt, N.E. of Butte Lake. WILLIAMS (1932), Anal. 36, p. 368.

4. Pale pyroxene andesite, N. side of Huckleberry Lake. WILLIAMS (1932), Anal. 5, p. 258.

5. Hypersthene andesite, S. slope of Badger Mountain. WILLIAMS (1932), Anal. 4, p. 240.

6. Platy pale grey andesite, Saddler Mountain. WILLIAMS (1932), Anal. 2, p. 223.

7. Platy pale grey andesite, Crystal Lake. WILLIAMS (1932), Anal. 1, p. 223.

8. Hornblende-mica dacite, Raker Peak. WILLIAMS (1932), Anal. 26, p. 365.

9. Hornblende-mica dacite, Lassen Peak. CLARKE (1915), Anal. A, p. 171.

(g) Crater Lake

The lavas of Crater Lake have been described by PATTON (1902) and WILLIAMS (1942). The variation diagram is shown in Fig. 8 and is similar to that for the Lesser Antilles, except that the acid lavas are richer in potassium. The estimated composition of the parental magma is given in Table 8, column 8, and Table 9, column 7. The lavas of Mount Shasta (WILLIAMS, 1934) also belong here.

Both these rock series are volcanic and, again, the curves of smooth variation are interpreted as representing the liquid line of descent during the differentiation of the parental magma.

VARIATION IN THE MAJOR AND TRACE ELEMENTS OF THE CALC-ALKALI ROCK SERIES

The data on which the following discussion is based are given in Tables 1 to 7 so far as the trace elements are concerned. For the major elements we had, of course, all the chemical data (which was recalculated on a water-free basis) available for each of the particular series. We shall confine our attention largely

Table 3. *Rocks of the Medicine Lake Highlands*

	A	B	C	1	2	3	4	5	6	7
Si ⁺⁴	227·10 ³	274·10 ³	334·10 ³	256·10 ³	275·10 ³	307·10 ³	341·10 ³	339·10 ³	342·10 ³	342·10 ³
Al ⁺³	97·10 ³	91·10 ³	78·10 ³	98·10 ³	95·10 ³	86·10 ³	74·10 ³	76·10 ³	75·10 ³	75·10 ³
Ti ⁺⁴	48·10 ²	54·10 ²	12·10 ²	54·10 ²	42·10 ²	42·10 ²	18·10 ²	18·10 ²	18·10 ²	18·10 ²
Fe ⁺³	21·10 ²	105·10 ²	49·10 ²	77·10 ²	35·10 ²	49·10 ²	56·10 ²	56·10 ²	7·10 ²	42·10 ²
Mg ⁺²	54·10 ³	20·10 ³	4·10 ³	35·10 ³	23·10 ³	11·10 ³	4·10 ³	2·10 ³	2·10 ³	2·10 ³
Fe ⁺²	68·10 ³	49·10 ³	16·10 ³	46·10 ³	45·10 ³	32·10 ³	12·10 ³	16·10 ³	19·10 ³	15·10 ³
Na ⁺¹	17·10 ³	26·10 ³	30·10 ³	22·10 ³	24·10 ³	30·10 ³	28·10 ³	29·10 ³	29·10 ³	28·10 ³
Ca ⁺²	83·10 ³	48·10 ³	18·10 ³	62·10 ³	51·10 ³	26·10 ³	13·10 ³	11·10 ³	11·10 ³	11·10 ³
K ⁺¹	8·10 ²	120·10 ²	290·10 ²	80·10 ²	140·10 ²	230·10 ²	330·10 ²	340·10 ²	330·10 ²	340·10 ²
B ⁺³	—	—	—	—	—	—	—	—	—	—
Ca ⁺³	15	20	15	20	15	15	15	15	15	15
Cr ⁺³	225	25	15	100	50	5	*	*	*	*
V ⁺³	175	125	30	100	130	20	10	10	10	8
Li ⁺¹	5	35	80	50	40	80	100	80	100	80
Ni ⁺²	225	*	15	70	40	*	*	*	*	*
Co ⁺²	50	15	5	25	25	*	*	*	*	*
Sc ⁺³	40	25	15	15	20	*	*	*	*	*
Zr ⁺⁴	50	175	250	65	200	250	250	175	175	175
Y ⁺³	20	25	25	*	25	30	35	35	35	35
La ⁺³	*	*	*	*	*	*	*	*	*	*
Sr ⁺²	400	1000	400	750	1000	300	150	150	150	150
Pb ⁺²	*	*	10	*	*	15	20	10	10	15
Ba ⁺²	20	350	1250	250	650	1000	1000	1500	1500	1000
Rb ⁺¹	*	50	200	50	75	200	300	300	250	250
Cs ⁺¹	—	—	*	—	—	*	—	—	—	—
Tl ⁺¹	*	*	*	*	*	*	*	*	*	*
Position	-6·0	+3·5	+11·8	-0·4	+3·2	+8·8	+13·0	+13·4	+13·4	+13·5
{ Fe	56	75	85	61	68	77	83	90	90	89
{ Mg	44	25	15	39	32	23	17	10	10	11
{ Fe	49	51	25	46	44	37	22	24	24	23
{ Mg	38	17	5	29	21	11	5	2	2	2
{ Alk	13	32	70	25	35	52	73	74	74	75

to the liquid line of descent, mentioning the accumulative types only when we have sufficient data. We have prepared diagrams illustrating the behaviour of the major, and some of the minor, elements along the liquid line of descent in the various series and these are given in Figs. 9, 10, 13 and 14. In these, the amount of a given element is plotted, by a modification of LARSEN'S method (1938) against $(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})$. LARSEN used oxides, and added iron in with calcium and magnesium. But if iron is added, it is impossible to show iron enrichment in a series satisfactorily. This does not affect the calc-alkali series but does arise in the alkali and tholeiitic series which will be the subject of later papers. By adopting the method given above, we are able to use the same basis of comparison for all the different rock series with which we shall deal. The scale for any given element is the same in all the diagrams, so that the behaviour of an element in any given rock series can be compared directly with that in any other.

The geochemistry of some igneous rock series

Table 3a. Medicine Lake Highlands

A	B	C	1	2	3	4	5	6	7	
0.15	0.22	0.19	0.20	0.16	0.17	0.20	0.20	0.20	0.20	Ga $\times$ 1000/Al
4.2	1.3	3.7	2.9	2.2	0.45	*	*	*	*	Cr $\times$ 1000/Mg
3.2	6.2	7.5	2.9	5.6	1.8	2.5	5.0	5.0	4.0	V $\times$ 1000/Mg
0.1	1.7	20	1.4	1.7	7	25	40	50	40	Li $\times$ 1000/Mg
4.2	*	3.7	2.0	1.7	*	*	*	*	*	Ni $\times$ 1000/Mg
0.9	0.7	1.2	0.7	1.1	*	*	*	*	*	Co $\times$ 1000/Mg
1.3	2.9	5.2	1.5	2.1	3.4	4.5	11	10	10	Fe/Mg
0.7	1.2	3.7	0.4	0.9	*	*	*	*	*	Sc $\times$ 1000/Mg
3.2	0.4	0.7	1.9	1.0	0.1	*	*	*	*	Cr $\times$ 1000/Fe
2.5	2.1	1.4	1.9	2.7	0.5	0.6	0.5	0.5	0.4	V $\times$ 1000/Fe
0.7	0.3	0.2	0.5	0.5	*	*	*	*	*	Co $\times$ 1000/Fe
0.6	0.4	0.7	0.3	0.4	*	*	*	*	*	Sc $\times$ 1000/Fe
0.2	0.5	1.4	*	0.5	1.1	2.7	3.2	3.2	3.2	Y $\times$ 1000/Ca
0.5	2.1	2.2	1.2	2.0	1.2	1.2	1.4	1.4	1.4	Sr $\times$ 100/Ca
0.5	1.7	0.9	1.2	1.5	0.6	0.3	0.3	0.3	0.3	Sr $\times$ 100/Ca + K
2.5	2.9	4.3	3.1	4.6	4.3	3.0	4.4	4.6	2.9	Ba $\times$ 100/K
*	0.4	0.7	0.6	0.5	0.8	0.9	0.9	0.8	0.8	Rb $\times$ 100/K

A. Warner basalt, 4 miles S.E. of East Sand Butte. ANDERSON (1941), Anal. 2, p. 387.

B. Platy olivine andesite, near S. end of Callahan lava flow. ANDERSON (1941), Anal. 1, p. 392.

C. Perlitic rhyolite, 1 mile S. of summit of Mount Hoffmann. ANDERSON (1941), Anal. 1, p. 399.

1. Basalt, inclusion in recent dacite of Glass Mountain rhyolite-dacite composite flow. ANDERSON (1941), Anal. 3, p. 390.

2. Basaltic andesite, porphyritic Modoc basalt, northern flank of highland. ANDERSON (1941), Anal. 5, p. 390.

3. Dacite, N.E. tongue of rhyolite-dacite composite flow. ANDERSON (1941), Anal. 1, p. 396.

4. Pumice ejecta from cone remnant, S. of Glass Mountain. ANDERSON (1941), Anal. 4, p. 399.

5. Rhyolite glass, summit of Glass Mountain. ANDERSON (1941), Anal. 3, p. 399.

6. Obsidian from flow, Glass Mountain. ANDERSON (1941), Anal. 6, p. 399.

7. Pumice from surface of obsidian flow, Glass Mountain. ANDERSON (1941), Anal. 5, p. 399.

Silicon and Oxygen (Figs. 9a to 9g)

In every calc-alkali rock series investigated in the present study, there is a steady rise in both silicon and oxygen with increasing positive value of the function $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$. The curves for silicon and oxygen are almost, but not quite, parallel and, in every case, the ratio of Si to O is 1 : 1.8 at the basic end of the liquid line of descent, rising to 1 : 1.4 at the extreme acid end. In terms of atomic proportions this corresponds very closely to a ratio Si_2O_6 at the basic end and Si_2O_5 at the acid end. It will be shown in a later paper that these ratios are different for the alkali igneous rock series.

Aluminium and Gallium (Figs. 9a to 9g)

The shapes of the curves for Al and Ga are very similar in each series, though the actual amounts of these elements vary to some extent. The ratio Ga/Al remains practically constant throughout each series and there is little evidence of enrichment in Ga with respect to Al except, in some instances, at the extreme acid end of a series. The average Ga $\times$ 1000/Al ratio varies a little with the series concerned being 0.20 for the Scottish Caledonian, 0.19 for the Medicine Lake series, 0.21

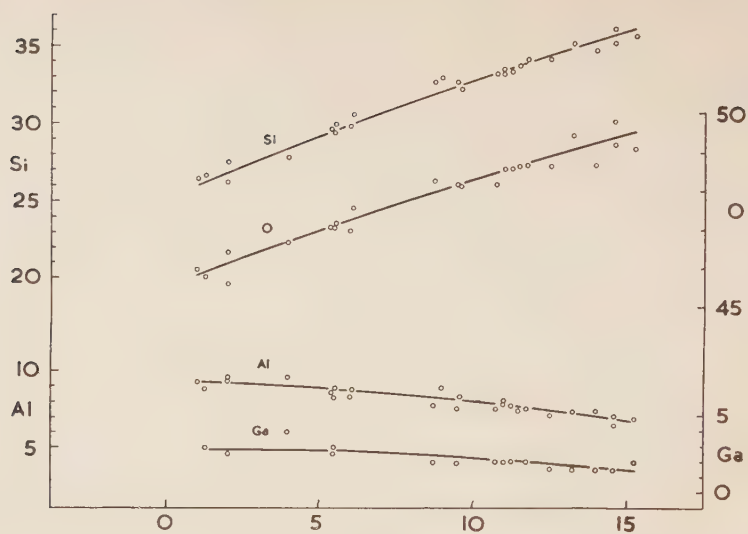


Fig. 9a. S. California batholith.

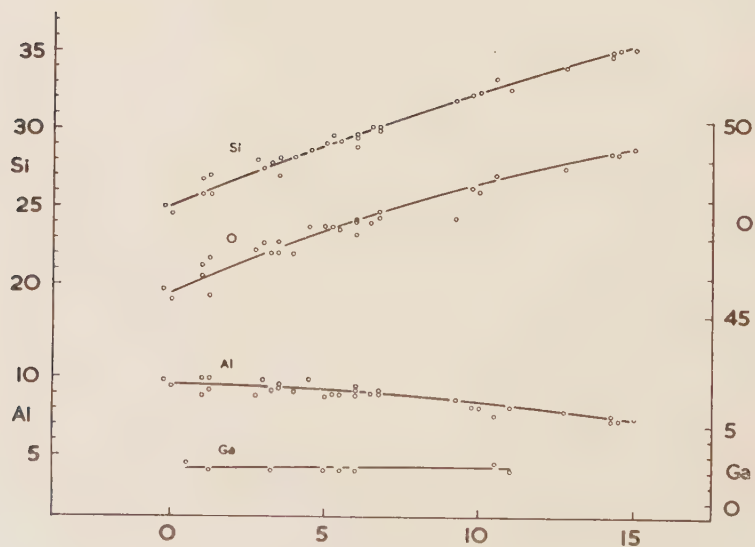


Fig. 9b. Lassen Peak

Fig. 9 a-g. Variation in Silicon, Oxygen, Aluminium and Gallium. Values in weight percent, with Ga $\times 1000$.

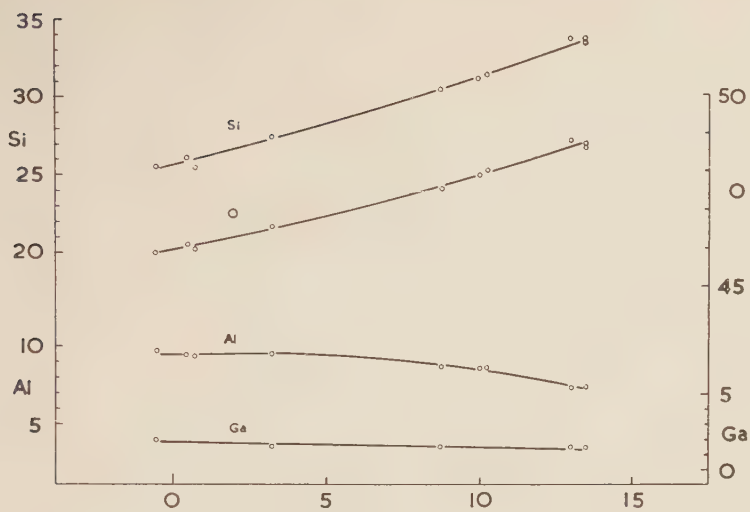


Fig. 9c. Medicine Lake Highlands

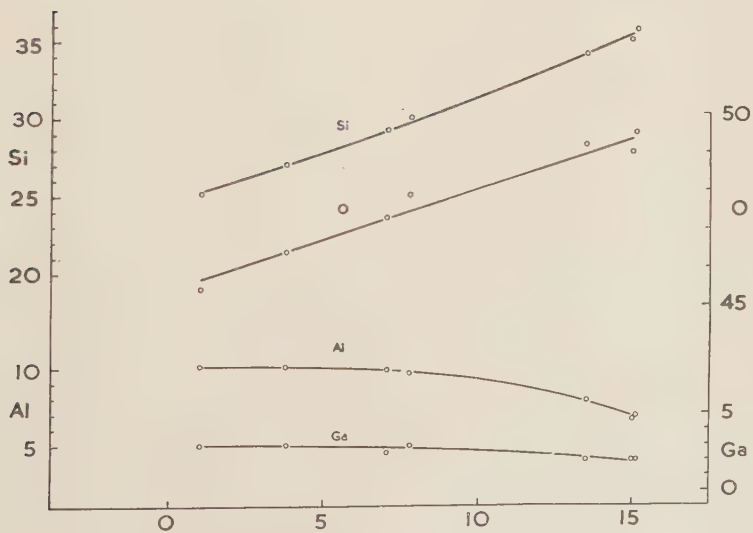


Fig. 9d. E. Central Sierra Nevada.

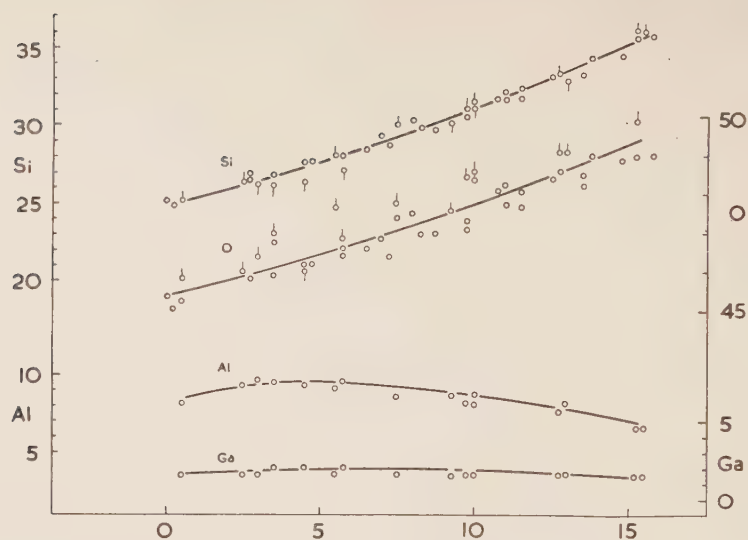


Fig. 9e. Scottish Caledonian.

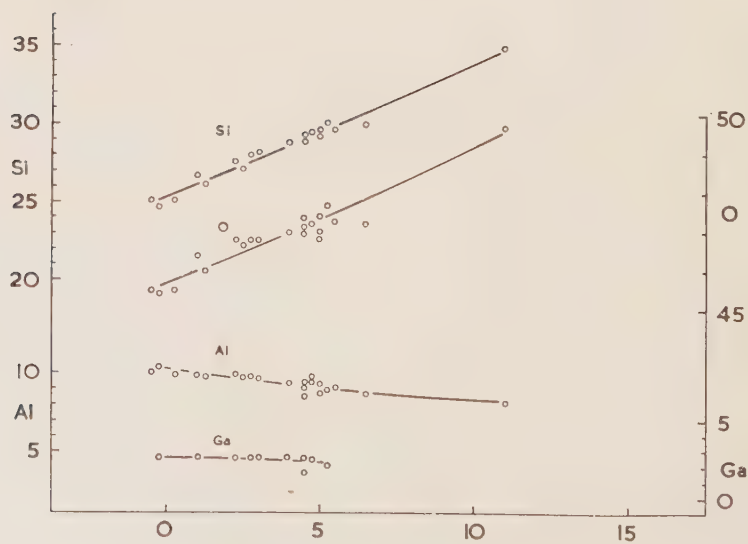


Fig. 9f. Lesser Antilles.

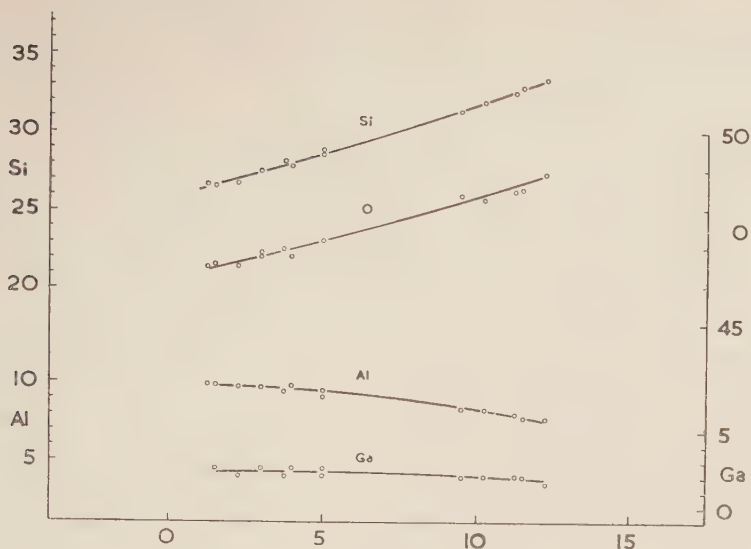


Fig. 9g. Crater Lake.

for Lassen Peak, 0.27 for the Southern California batholith, 0.28 for the E. Central Sierra Nevada series, 0.23 for Crater Lake and 0.25 for the Lesser Antilles.

Magnesium, Nickel, Lithium, Iron, Cobalt, Chromium, Vanadium, Titanium, Scandium (Figs. 10a to 10g)

These elements, with the exception of Li, all behave in the same general way in every series and gradually decrease in amount as the rocks become more acid. Lithium, on the other hand increases in amount in the same direction.

The original parental magmas of the different series vary in their content of Mg and, to a less extent, of Fe (see Tables 8 and 9) and this affects the amounts of Cr, V, Ni and Co present. In general, it may be stated, that the contents of Cr and Ni tend to be relatively high in the more magnesian parent magmas and to decrease in amount as the parent magma becomes less magnesian. Moreover, the decrease is greater than it would be for a member of a more magnesian series having the same content of Mg. This is clearly shown in Figs. 11 and 12 where the contents of Cr, V, Ni, Co and Fe are plotted against Mg for the different series.

V increases in amount as the parental magma becomes less magnesian. Co does not vary much in absolute amount but the ratio Co/Mg tends to be greater as the Mg content of the parental magma decreases.

The decreasing content of Ni, and increasing content of Co in relation to Mg in the parental magmas, has an interesting effect on the behaviour of the curves for Ni and Co in the variation diagrams. In the series with the most magnesian parental magma (Scottish Caledonian, Fig. 10e) the curve for Ni lies above that for Co, until the extreme acid end of the diagram is reached where they both drop

Table 4. *Rocks of East Central Sierra Nevada (calc-alkali series)*

	1	2	3	4	5	6	7	8
Si ⁺⁴	252·10 ³	271·10 ³	293·10 ³	302·10 ³	344·10 ³	353·10 ³	360·10 ³	373·10 ³
Al ⁺³	102·10 ³	101·10 ³	99·10 ³	97·10 ³	79·10 ³	66·10 ³	68·10 ³	56·10 ³
Ti ⁺⁴	42·10 ³	36·10 ³	36·10 ³	36·10 ³	12·10 ²	6·10 ²	6·10 ²	6·10 ²
Fe ⁺³	17·10 ³	24·10 ³	7·10 ³	18·10 ³	4·10 ³	4·10 ³	3·10 ³	1·10 ³
Mg ⁺²	27·10 ³	20·10 ³	14·10 ³	7·10 ³	2·10 ³	5·10 ³	1·10 ³	3·10 ²
Fe ⁺²	50·10 ³	29·10 ³	29·10 ³	14·10 ³	11·10 ³	9·10 ³	3·10 ³	20·10 ³
Na ⁺¹	27·10 ³	27·10 ³	24·10 ³	27·10 ³	24·10 ³	25·10 ³	27·10 ³	13·10 ³
Ca ⁺²	56·10 ³	46·10 ³	35·10 ³	34·10 ³	10·10 ³	5·10 ³	5·10 ³	2·10 ³
K ⁺¹	10·10 ³	13·10 ³	21·10 ³	17·10 ³	33·10 ³	42·10 ³	37·10 ³	39·10 ³
B ⁺³	—	—	—	—	—	—	—	—
Ga ⁺³	30	30	25	30	20	20	20	10
Cr ⁺³	20	25	40	5	*	*	*	*
V ⁺³	200	200	100	80	30	5	*	20
Li ⁺¹	20	25	15	25	50	30	50	50
Ni ⁺²	10	5	30	5	*	*	*	*
Co ⁺²	20	20	15	10	*	*	*	*
Sc ⁺³	*	*	*	*	*	*	*	*
Zr ⁺⁴	125	200	150	100	80	100	50	50
Y ⁺³	20	30	20	20	20	30	*	*
La ⁺³	*	*	*	*	50	100	50	*
Sr ⁺²	1000	1500	1500	1500	1000	200	2	50
Pb ⁺²	?10	*	25	20	50	50	30	30
Ba ⁺²	1000	1500	1500	1500	2500	800	5	1250
Rb ⁺¹	50	50	200	100	250	250	300	125
Cs ⁺¹	*	*	?	*	?15	?	15	*
Position	+1·1	+3·7	+7·0	+7·7	+13·6	+15·0	+15·1	+16·1
(Fe	71	73	72	82	88	72	86	99
(Mg	29	27	28	18	12	28	14	1
(Fe	51	47	38	39	20	15	8	29
(Mg	21	18	15	8	3	6	1	tr.
(Alk	28	35	47	53	77	79	91	71

below the limits of sensitivity. In the next most magnesian series (Medicine Lake Highlands, Fig. 10c; and Crater Lake, Fig. 10g) Ni still lies above Co but both drop below the limits of sensitivity at an earlier stage. Next comes the Lassen Peak series (Fig. 10b) where the curves are closer together and where the Ni curve falls below the Co curve just before the limit of sensitivity is reached. In the case of the S. California batholith (Fig. 10a) Ni starts above Co, but the curve soon falls below the Co curve. In the two least magnesian series (E. Central Sierra Nevada, Fig. 10d and Lesser Antilles, Fig. 10f) the Co curve lies above the Ni curve throughout. Moreover, the distance apart of the curves is greater in the Lesser Antilles series than in the East Central Sierra Nevada series. One further result should be noted, namely that Ni falls below the limits of sensitivity earlier and earlier in each series.

Scandium follows iron, in the sense that it tends to be slightly more abundant in the least magnesian parental magmas. But in every series it soon falls below the limits of sensitivity, so that its behaviour cannot be traced satisfactorily.

The geochemistry of some igneous rock series

Table 4a. *East Central Sierra Nevada (calc-alkali series)*

	1	2	3	4	5	6	7	8
Ga $\times$ 1000/Al	0.29	0.30	0.25	0.31	0.25	0.30	0.29	0.18
Cr $\times$ 1000/Mg	0.7	1.2	(2.9)	0.7	*	*	*	*
V $\times$ 1000/Mg	7.4	10.0	7.1	11.4	15.0	1.0	*	66.7
Li $\times$ 1000/Mg	0.7	1.2	1.1	3.6	25.0	6.0	50.0	167
Ni $\times$ 1000/Mg	0.3	0.3	(2.1)	0.7	*	*	*	*
Co $\times$ 1000/Mg	0.7	1.0	1.1	1.4	*	*	*	*
Fe/Mg	2.5	2.7	(2.6)	4.6	7.5	2.6	6.0	70.0
Sc $\times$ 1000/Mg	*	*	*	*	*	*	*	*
Cr $\times$ 1000/Fe	0.3	0.5	(1.1)	0.2	*	*	*	*
V $\times$ 1000/Fe	3.0	3.8	2.8	2.5	2.0	0.4	*	1.0
Co $\times$ 1000/Fe	3.0	0.4	0.4	0.3	*	*	*	*
Sc $\times$ 1000/Fe	*	*	*	*	*	*	*	*
Y $\times$ 1000/Ca	0.4	0.6	0.6	0.6	2.0	6.0	*	*
Sr $\times$ 100/Ca	1.8	3.3	4.3	4.4	10.0	4.0	0.04	2.5
Sr $\times$ 100/Ca + K	1.5	2.5	2.7	2.9	2.3	0.4	0.00	0.1
Ba $\times$ 100/K	10.0	11.5	7.1	8.9	7.6	1.9	0.01	3.2
Rb $\times$ 100/K	0.5	0.4	1.0	0.6	0.8	0.6	0.8	0.3

1. Pyroxene andesite intrusion. (CURTIS, No. 9-28-45.)

2. Pyroxene andesite flow. (CURTIS, No. 7-24-46.)

3. Dacite bomb. (CURTIS, No. 17-28-45.)

4. Dacite dome. (CURTIS, No. 22-28-45.)

5. Late? rhyolite flow. (CURTIS, No. 15-24-156.)

6. Older rhyolite flow. (SLEMMONS, No. 1-177.)

7. Latest rhyolite dome. (HALSEY, No. 10C.)

8. Siliceous injection in rhyolite dome (lies off the liquid line of descent). (CURTIS, No. M-1.)

Turning now to the relationship between the trace elements and the major constituents, the general behaviour is the same in each series (Tables 1a to 7a). The ratios Cr/Mg, Ni/Mg, Cr/Fe, V/Fe decrease in every case as we pass to more acid rocks. The ratio V/Mg is somewhat variable but shows a tendency to increase in the same direction. Co/Mg and Co/Fe remain more or less constant but show a slight tendency to decrease as the more acid rocks in each series are approached. Moreover, the average ratio Co $\times$ 1000/Mg has practically the same value (about 0.9) in each series, which agrees well with the ratio Co/MgO = 0.00066 found by SANDELL and GOLDICH (1943) who were the first to notice the constancy of this ratio. The ratio Co $\times$ 1000/Fe (total) averages 0.4 for each series, the range being 0.34 to 0.49. The ratio Li/Mg increases steadily in each series in the same direction (STROCK, 1936). These changes are what would be expected to occur on the basis of the size and valency of the ions concerned.

Calcium and Strontium (Figs. 13a to 13g)

With the exception of the S. California batholith, which is remarkably low in strontium, the Ca and Sr contents of the parental magmas do not show a great deal of variation (Table 9).

Calcium decreases steadily in every series as the value of the function $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, and the decrease is virtually linear. Stron-

Table 6. *Rocks of the Lesser Antilles*

	1	2	3	4	5	6	7	8	9	10	11	12	13
Si ⁺⁴	244·10 ³	246·10 ³	263·10 ³	267·10 ³	276·10 ³	280·10 ³	282·10 ³	287·10 ³	288·10 ³	294·10 ³	290·10 ³	283·10 ³	301·10 ³
Al ⁺³	102·10 ³	104·10 ³	91·10 ³	98·10 ³	99·10 ³	97·10 ³	96·10 ³	94·10 ³	94·10 ³	91·10 ³	93·10 ³	109·10 ³	89·10 ³
Ti ⁺⁴	36·10 ²	54·10 ²	72·10 ²	42·10 ²	24·10 ²	30·10 ²	30·10 ²	24·10 ²	30·10 ²	18·10 ²	24·10 ²	36·10 ²	18·10 ²
Fe ⁺³	19·10 ³	20·10 ³	27·10 ³	17·10 ³	16·10 ³	17·10 ³	15·10 ³	15·10 ³	15·10 ³	9·10 ³	15·10 ³	27·10 ³	26·10 ³
Mg ⁺²	33·10 ³	23·10 ³	25·10 ³	22·10 ³	20·10 ³	17·10 ³	18·10 ³	19·10 ³	14·10 ³	15·10 ³	14·10 ³	5·10 ³	13·10 ³
Fe ⁺²	44·10 ³	45·10 ³	26·10 ³	39·10 ³	35·10 ³	34·10 ³	32·10 ³	33·10 ³	33·10 ³	33·10 ³	32·10 ³	9·10 ³	14·10 ³
Na ⁺¹	19·10 ³	24·10 ³	22·10 ³	20·10 ³	17·10 ³	23·10 ³	22·10 ³	21·10 ³	27·10 ³	24·10 ³	26·10 ³	26·10 ³	25·10 ³
Ca ⁺²	76·10 ³	69·10 ³	70·10 ³	62·10 ³	58·10 ³	54·10 ³	54·10 ³	47·10 ³	46·10 ³	49·10 ³	46·10 ³	54·10 ³	43·10 ³
K ⁺¹	66·10 ²	83·10 ²	75·10 ²	58·10 ²	75·10 ²	58·10 ²	83·10 ²	91·10 ²	83·10 ²	108·10 ²	83·10 ²	108·10 ²	91·10 ²
B ⁺³	*	5	20	*	—	—	*	—	—	—	—	—	5
Ga ⁺³	30	25	25	25	25	25	25	25	20	25	25	25	20
Cr ⁺³	35	5	20	15	5	*	5	*	*	*	*	*	*
V ⁺³	400	300	150	200	150	150	170	100	100	100	100	50	100
Li ⁺¹	5	20	20	15	15	30	30	45	45	40	45	30	45
Ni ⁺²	20	5	5	10	5	*	*	*	*	*	*	*	*
Co ⁺²	35	30	25	25	20	15	20	15	15	10	10	5	10
Sc ⁺³	50	20	30	30	20	*	*	*	*	*	*	*	*
Zr ⁺⁴	80	85	100	100	100	100	125	100	90	75	75	75	100
Y ⁺³	20	20	25	20	20	20	25	20	20	20	20	25	20
La ⁺³	*	*	*	*	*	*	*	*	*	*	*	*	*
Sr ⁺²	500	750	400	300	250	300	400	300	300	300	300	350	250
Pb ⁺²	*	*	10	*	*	*	10	10	10	10	10	15	*
Ba ⁺²	75	100	400	150	150	150	200	200	150	200	200	250	300
Rb ⁺¹	10	20	50	20	20	20	25	35	35	45	30	45	40
Cs ⁺¹	*	*	*	*	*	*	*	*	*	*	*	*	*
Tl ⁺¹	*	*	*	*	*	*	*	*	*	*	*	*	*
Position	-2·1	-0·2	+0·1	+1·1	+2·2	+2·8	+3·0	+3·9	+4·4	+4·5	+4·5	+4·6	+5·3
{ Fe	66	74	68	72	72	75	72	72	77	74	77	88	75
{ Mg	34	26	32	28	28	25	28	28	23	26	23	12	25
{ Fe	52	54	50	54	54	52	49	49	50	46	49	46	46
{ Mg	27	19	23	21	21	18	19	19	14	16	15	6	15
{ Alk	21	27	27	25	25	30	32	32	36	38	36	48	39

tium, however, behaves in two different ways. It may increase gradually in amount to a maximum value and then decrease rapidly to a very low value, as the value of the function $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases. This is shown by the E. Central Sierra Nevada series (Fig. 13d), by the Scottish Caledonian series (Fig. 13e) and probably would be shown also by the Lassen Peak series (Fig. 13b) but, unfortunately, we have no analysed specimens of the most acid rocks to test this.

On the other hand, strontium may decrease, like Ca, as the function $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, and the curves for Ca and Sr tend to converge as the more acid rocks are approached. This state of affairs is shown by the Medicine Lake Highlands series (Fig. 13c), the S. California batholith (Fig. 13a), the Crater Lake Series (Fig. 13g) and that of the Lesser Antilles (Fig. 13f) though here, again, we have been unable to obtain a sample of the most acid rock type described.

The geochemistry of some igneous rock series

Table 6a. *Lesser Antilles*

	1	2	3	4	5	6	7	8	9	10	11	12	13
< 1000/Al	0.29	0.24	0.27	0.26	0.25	0.26	0.26	0.27	0.22	0.27	0.27	0.23	0.22
< 1000/Mg	1.1	0.2	0.8	0.7	0.25	*	0.3	*	*	*	*	*	*
1000/Mg	12	13	6	9	7.5	9	9	5.3	7	7	7	10	7.7
1000/Mg	0.15	0.9	0.8	0.7	0.8	1.8	1.7	2.4	3.2	2.7	3.2	6.0	3.5
< 1000/Mg	0.6	0.2	0.2	0.5	0.25	*	*	*	*	*	*	*	*
< 1000/Mg	1.1	1.3	1.0	1.1	1.0	0.9	1.1	0.8	1.1	0.7	0.7	1.0	0.8
Mg	1.9	2.8	2.1	2.5	2.5	3.0	2.6	2.5	3.4	2.8	3.4	7.2	3.1
1000/Mg	1.5	0.9	1.2	1.4	1.0	*	*	*	*	*	*	*	*
< 1000/Fe	0.6	0.1	0.4	0.3	0.1	*	0.1	*	*	*	*	*	*
1000/Fe	6.3	4.6	2.8	3.6	2.9	2.9	3.6	2.1	2.1	2.4	2.1	1.4	2.5
< 1000/Fe	0.6	0.5	0.5	0.4	0.4	0.3	0.4	0.3	0.3	0.2	0.2	0.1	0.2
< 1000/Fe	0.8	0.3	0.6	0.6	0.4	*	*	*	*	*	*	*	*
1000/Ca	0.3	0.3	0.4	0.3	0.3	0.4	0.5	0.4	0.4	0.4	0.4	0.5	0.5
100/Ca	0.7	1.1	0.6	0.5	0.4	0.6	0.7	0.6	0.7	0.6	0.7	0.6	0.6
100/Ca + K	0.6	1.0	0.5	0.4	0.4	0.5	0.6	0.5	0.6	0.5	0.6	0.5	0.5
< 100/K	1.1	1.2	(5.3)	2.6	2.0	2.6	2.4	2.2	1.8	1.9	2.4	2.3	3.3
< 100/K	0.2	0.2	(0.7)	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4

Olivine basalt (accumulative), S. of Soufriere Hill, Montserrat. MACGREGOR (1938), Anal. 7, p. 74.

Olivine basalt, 500 yds. W. of Shoe Rock, Montserrat. MACGREGOR (1938), Anal. 6, p. 74.

Dacitoid, near Morne des Cadets, Martinique. LACROIX (1924), p. 394.

Pyroxene-bandaite, Centre Hills, Montserrat. MACGREGOR (1938), Anal. 5, p. 74.

Pyroxene bandaite, Silver Hill, Montserrat. MACGREGOR (1938), Anal. 4, p. 74.

Hornblende-pyroxene bandaite, Castles Peak, Montserrat. MACGREGOR (1938), Anal. 3, p. 74.

Hornblende-pyroxene bandaite, near Old Fort Point, Montserrat. MACGREGOR (1938), Anal. 2, p. 74.

8. Dacitoid, summit of Mt. Pelée, Martinique. LACROIX (1924), p. 394.

9. Dacitoid pumice, eruption of July 1902, Mt. Pelée, Martinique. LACROIX (1924), p. 394.

10. Dacite, eruption of January 1903, Mt. Pelée, Martinique. LACROIX (1924), p. 394.

11. Dacite, eruption of 1906, Mt. Pelée, Martinique. (Unpublished analysis by J. H. SCOON.)

12. Dacite, neighbourhood of St. Pierre, Martinique. (Unpublished analysis by J. H. SCOON.)

13. Acid hornblende-pyroxene bandaite, near Landing Bay, Montserrat. MACGREGOR (1938), Anal. 1, p. 74.

This difference of behaviour must be correlated with the removal of Sr by early crystallizing minerals, in effect by plagioclase, as the Ca-bearing ferromagnesian minerals carry very little Sr (NOCKOLDS and MITCHELL, 1948). If much early crystallizing plagioclase feldspar is removed from the system, then the Sr will decrease in the residual liquid, whereas if relatively little is being removed, then the Sr content of the residual liquid will increase.

The ratio Sr/Ca increases continuously in the E. Central Sierra Nevada series, the Scottish Caledonian series, the rocks of the S. California batholith, the Lassen Peak series (as far as traced) and the Crater Lake series, but falls at the extreme acid end of the first two. It remains more or less constant in the Medicine Lake Highlands series and in that of the Lesser Antilles (as far as traced). The ratio Sr/Ca + K increases in the case of the Lassen Peak series (as far as traced), the E. Central Sierra Nevada series, the rocks of the S. California batholith and the Scottish Caledonian series, but decreases in the last three as the more acid rocks are approached. In the Medicine Lake Highlands series the ratio remains more or less constant at first, but decreases again when the more acid rocks are reached.

Table 7. *Rocks of Crater Lake, Oregon*

	1	2	3	4	5	6	7	8	9	10	11	12	13
Si ⁺⁴	250·10 ³	267·10 ³	268·10 ³	276·10 ³	282·10 ³	280·10 ³	288·10 ³	291·10 ³	317·10 ³	322·10 ³	329·10 ³	333·10 ³	338·10 ³
Al ⁺³	89·10 ³	99·10 ³	98·10 ³	96·10 ³	95·10 ³	98·10 ³	95·10 ³	91·10 ³	84·10 ³	84·10 ³	81·10 ³	79·10 ³	78·10 ³
Ti ⁺⁴	7·10 ³	5·10 ³	7·10 ³	4·10 ³	3·10 ³	2·10 ³	4·10 ³	4·10 ³	4·10 ³	3·10 ³	3·10 ³	2·10 ³	2·10 ³
Fe ⁺³	27·10 ³	15·10 ³	20·10 ³	19·10 ³	14·10 ³	13·10 ³	13·10 ³	17·10 ³	13·10 ³	16·10 ³	13·10 ³	10·10 ³	9·10 ³
Mg ⁺²	43·10 ³	26·10 ³	24·10 ³	22·10 ³	21·10 ³	19·10 ³	17·10 ³	19·10 ³	8·10 ³	6·10 ³	4·10 ³	4·10 ³	3·10 ³
Fe ⁺²	28·10 ³	33·10 ³	26·10 ³	26·10 ³	27·10 ³	30·10 ³	26·10 ³	21·10 ³	14·10 ³	7·10 ³	9·10 ³	10·10 ³	8·10 ³
Na ⁺¹	27·10 ³	29·10 ³	30·10 ³	29·10 ³	31·10 ³	33·10 ³	33·10 ³	30·10 ³	33·10 ³	39·10 ³	39·10 ³	39·10 ³	38·10 ³
Ca ⁺²	61·10 ³	54·10 ³	52·10 ³	49·10 ³	46·10 ³	46·10 ³	41·10 ³	41·10 ³	24·10 ³	20·10 ³	16·10 ³	15·10 ³	11·10 ³
K ⁺¹	108·10 ²	66·10 ²	100·10 ²	100·10 ²	108·10 ²	108·10 ²	116·10 ²	141·10 ²	199·10 ²	207·10 ²	216·10 ²	224·10 ²	232·10 ²
B ⁺³	—	*	10	15	*	5	—	—	—	15	—	10	—
Ga ⁺³	20	25	20	25	20	25	25	20	20	20	20	20	15
Cr ⁺³	300	100	80	70	60	60	40	80	10	5	1	*	*
V ⁺³	180	100	120	150	150	120	120	150	60	50	45	30	30
Li ⁺¹	20	15	20	15	20	20	20	25	20	35	40	40	35
Ni ⁺²	100	70	50	50	50	40	30	50	10	5	*	*	*
Co ⁺³	30	25	20	15	20	20	15	20	5	*	*	*	*
Sc ⁺³	110	110	110	110	110	110	110	110	110	*	*	*	*
Zr ⁺⁴	150	70	100	120	100	120	100	150	200	175	175	175	175
Y ⁺³	15	15	20	20	20	20	20	20	20	20	20	30	30
La ⁺³	*	*	*	*	*	*	*	*	*	*	*	*	*
Sr ⁺²	1500	1200	1000	900	1000	750	800	750	700	700	650	650	650
Pb ⁺²	*	*	*	*	*	*	*	*	*	*	110	110	*
Ba ⁺²	500	250	450	350	550	500	500	500	850	750	800	1000	1250
Rb ⁺¹	15	10	20	20	25	20	20	25	60	100	60	100	100
Cs ⁺¹	*	*	*	*	*	*	*	*	*	*	*	*	*
Tl ⁺¹	*	*	*	*	*	*	*	*	*	*	*	*	*
Position	-1·0	+1·6	+2·3	+3·1	+3·8	+3·9	+5·0	+5·1	+9·4	+10·2	+11·2	+11·4	+12·5
{ Fe	56	59	66	67	66	69	70	67	77	79	85	85	85
{ Mg	44	41	34	33	34	31	30	33	23	21	15	15	15
{ Fe	40	38	42	42	40	41	39	38	31	26	25	24	21
{ Mg	32	26	22	21	20	18	17	19	9	7	5	4	4
{ Alk	28	36	36	37	40	41	44	43	60	67	70	72	75

Having regard to the ionic radii of Sr and Ca, it may be expected that Sr, present for the most part in plagioclase among the Ca-bearing minerals, would be concentrated relative to Ca in the later rocks of a series. On the other hand Sr enters certain potassium-bearing minerals, especially potash feldspars, and then it would be expected to concentrate in the early formed potash feldspar: It is the interplay of these two factors that is responsible for the behaviour of the Sr/Ca + K ratio, the first being dominant in the earlier stages, the second becoming gradually more important and finally dominant in the latest stages thus leading to a decrease in the Sr/Ca + K ratio.

The ratio Sr/Ca + K remains practically constant throughout in the Crater Lake series and in that of the Lesser Antilles (as far as traced). This is due to the fact that potassium is not concentrated to the same extent in these two series as in

The geochemistry of some igneous rock series

Table 7a. Crater Lake

	1	2	3	4	5	6	7	8	9	10	11	12	13
× 1000/Al	0.22	0.25	0.20	0.26	0.21	0.26	0.26	0.22	0.24	0.24	0.25	0.25	0.19
× 1000/Mg	7.0	3.8	3.3	3.2	2.9	3.2	2.4	4.2	1.2	0.8	0.25	*	*
× 1000/Mg	4.2	3.8	5.0	6.8	7.1	6.3	7.1	7.9	7.5	8.3	11	8	10
× 1000/Mg	0.5	0.6	0.8	0.7	1.0	1.1	1.2	1.3	2.5	5.8	10	10	12
× 1000/Mg	2.3	2.7	2.1	2.3	2.4	2.1	1.8	2.6	1.2	0.7	*	*	*
× 1000/Mg	0.7	1.0	0.8	0.7	1.0	1.1	0.9	1.1	0.6	*	*	*	*
Mg	1.3	1.8	1.9	2.0	2.0	2.3	2.3	2.0	3.4	3.8	5.5	5.0	5.7
× 1000/Mg	—	—	—	—	—	—	—	—	—	*	*	*	*
× 1000/Fe	5.5	2.1	1.7	1.6	1.5	1.4	1.0	2.1	0.4	0.2	*	*	*
× 1000/Fe	3.3	2.1	2.6	3.3	3.7	2.8	3.1	3.9	2.2	2.2	2.0	1.5	1.8
× 1000/Fe	0.5	0.5	0.4	0.3	0.5	0.5	0.4	0.5	0.2	*	*	*	*
× 1000/Fe	—	—	—	—	—	—	—	—	—	*	*	*	*
× 1000/Ca	0.25	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.8	1.0	1.3	2.0	2.7
× 100/Ca	2.5	2.2	1.9	1.8	2.2	1.6	1.95	1.8	2.9	3.5	4.1	4.3	5.5
× 100/Ca + K	2.1	2.0	1.6	1.5	1.8	1.3	1.5	1.4	1.6	1.7	1.7	1.8	1.8
× 100/K	4.5	3.8	4.5	3.5	5.0	4.5	4.3	3.6	4.2	3.6	3.7	4.5	5.4
× 100/K	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.5	0.3	0.5	0.4

Basalt (accumulative), base of Red Cone. CLARKE (1915), J. p. 199.
 Hypersthene basalt, Anna Creek. CLARKE (1915), Anal. K, p. 200.
 Dark secretion, summit of Llao Rock. CLARKE (1915), Anal. I, p. 199.
 Pyroxene andesite, lake level, under Llao Rock. CLARKE (1915), Anal. E, p. 199.
 Pyroxene andesite, dyke, N.W. portion of crater rim. CLARKE (1915), Anal. F, p. 199.
 Pyroxene andesite, W. edge of Wizard Island. CLARKE (1915), Anal. G, p. 199.
 Pyroxene andesite, crater rim, just S. of "The Watchman." CLARKE (1915), Anal. G, p. 199.

8. Pyroxene andesite, Palisades, N.E. portion of crater rim. CLARKE (1915), Anal. H, p. 199.
 9. Light coloured secretion, southern rim of crater. CLARKE (1915), Anal. N, p. 200.
 10. Hypersthene dacite, near "Wine Glass" Grotto Cove. CLARKE (1915), Anal. B, p. 199.
 11. Hypersthene dacite, head of Cleetwood Cove. CLARKE (1915), Anal. D, p. 199.
 12. Hypersthene dacite, S. edge of Llao Rock flow. CLARKE (1915), Anal. A, p. 199.
 13. Hypersthene dacite, small dyke, below Llao Rock. CLARKE (1915), Anal. C, p. 199.

the others. with the result that the effect of Sr substitution of K in potash feldspar does not become dominant over the Sr substitution of Ca in plagioclase feldspar.

Yttrium

The Scottish Caledonian series cannot be used for a discussion of yttrium, as the limit of sensitivity for the method of determination used for that series is 30 ppm and the yttrium content rarely rises above this. But in all the other series the Y/Ca ratio increases steadily as the more acid rocks are approached. With regard to the absolute amounts of yttrium present, this tends to be constant throughout a large portion of the range of any one series, though in some series it increases at the acid end (Medicine Lake Highlands, S. California batholith, Crater Lake). There is, however, a decrease at the extreme acid end of the E. Central Sierra Nevada series.

The initial yttrium content of the parental magma is apparently a function of the Fe/Mg ratio, and yttrium falls below the limits of sensitivity in the more magnesian parental magmas (see Table 9).

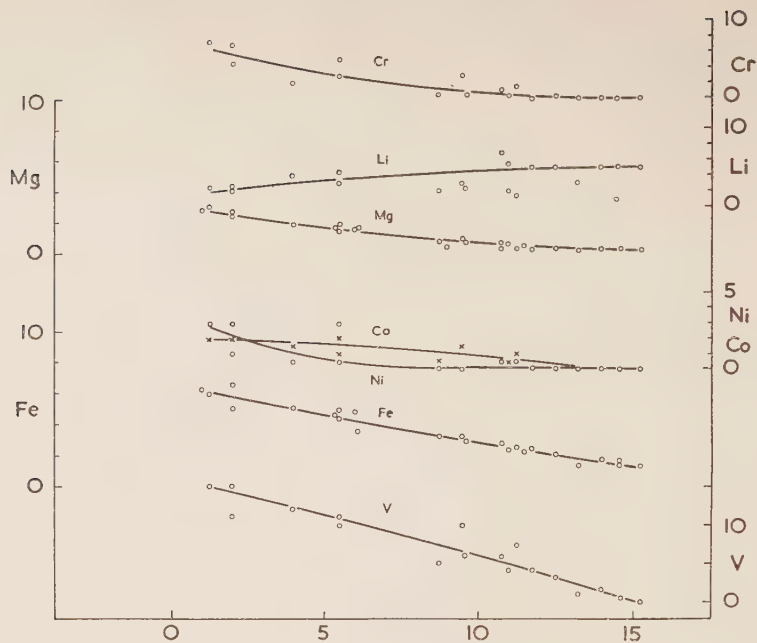


Fig. 10a. S. California batholith.

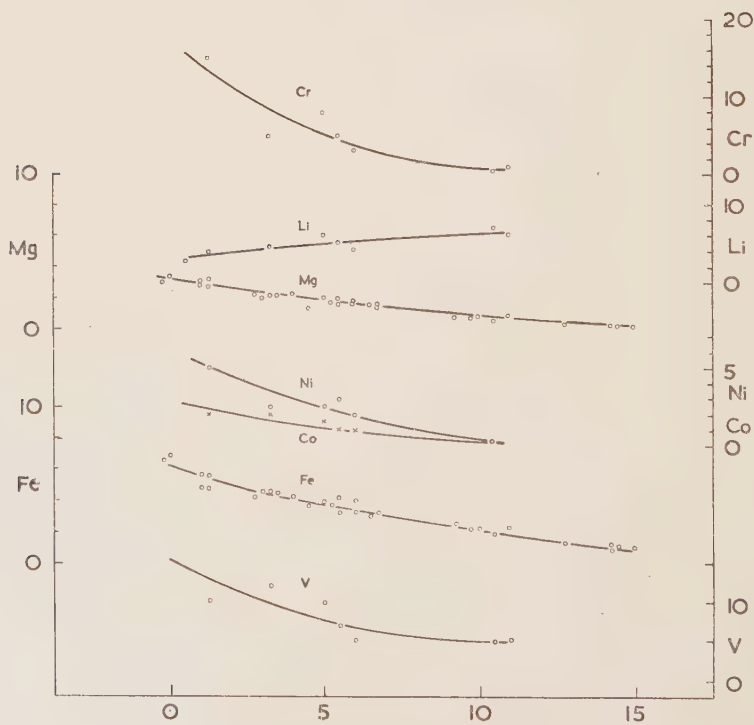


Fig. 10b. Lassen Peak.

Fig. 10 a-g. Variation in Chromium, Lithium, Magnesium, Nickel, Cobalt, Iron and Vanadium. Values in weight percent, with Cr, Li, Ni, Co and V $\times 1000$.

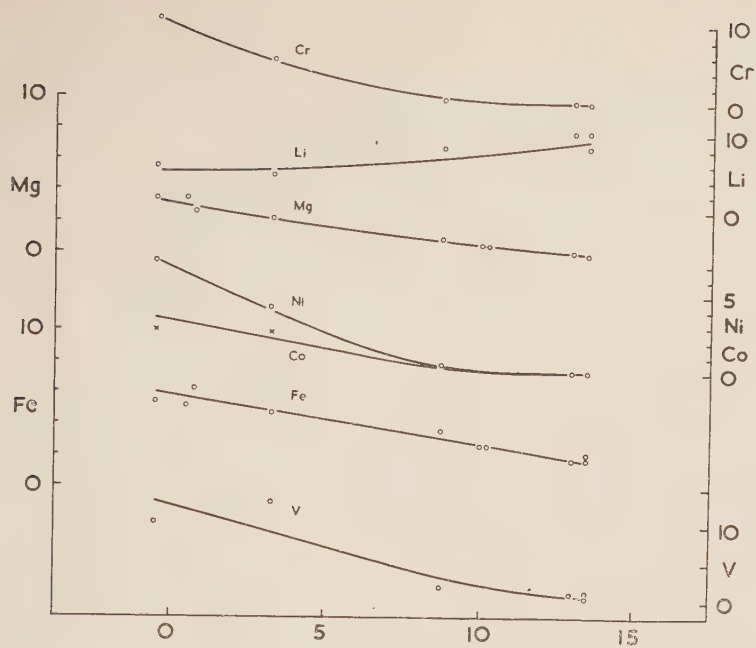


Fig. 10c. Medicine Lake Highlands.

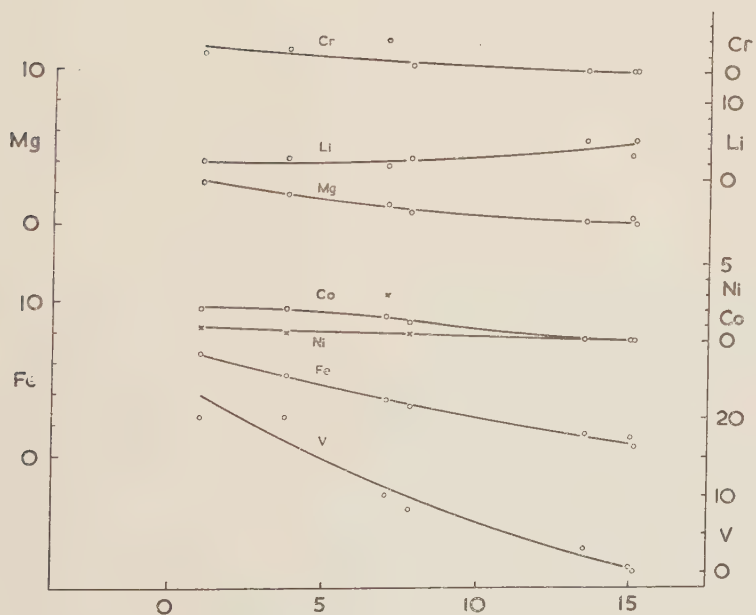
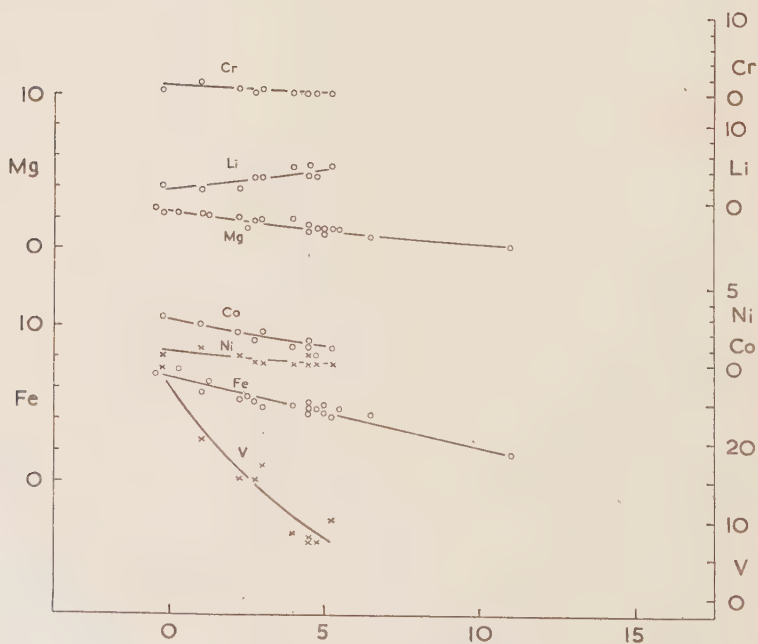
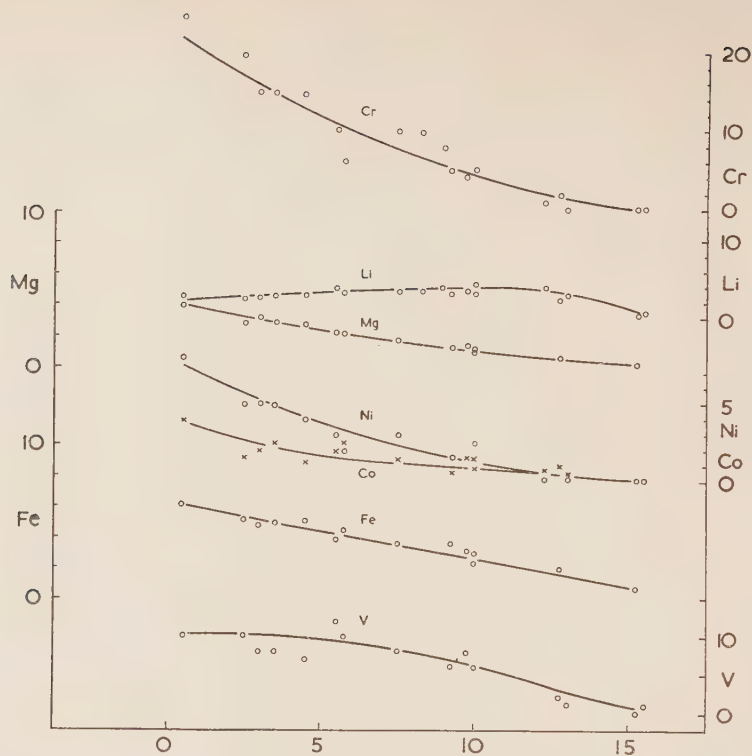


Fig. 10d. E. Central Sierra Nevada.



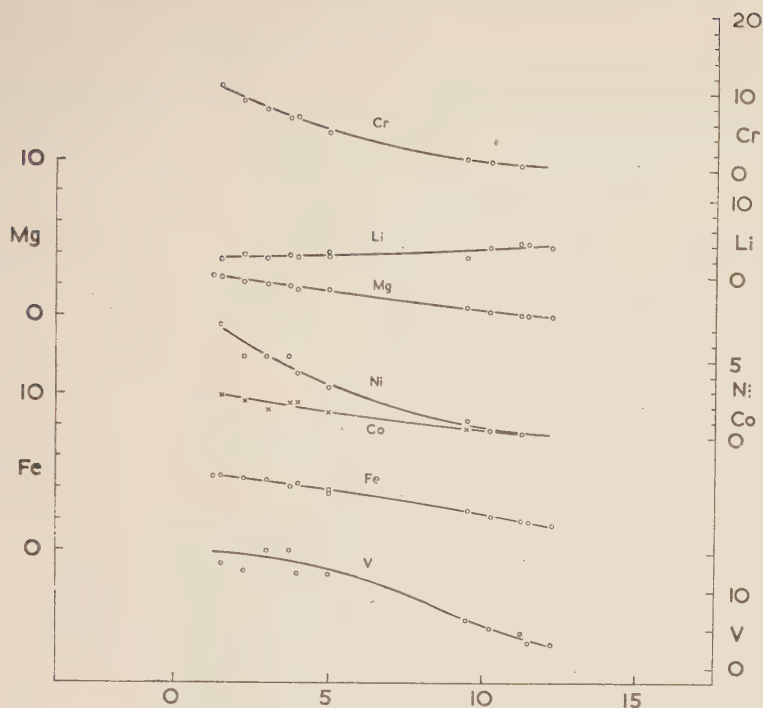


Fig. 10g. Crater Lake.

Lanthanum

Lanthanum rarely rises above the limit of sensitivity (40 ppm) in any of the rock series under investigation. It does, however, appear in the most acid members of the E. Central Sierra Nevada series, the Southern California batholith series, and the Scottish Caledonian series.

Sodium (Figs. 13a to 13g)

Sodium behaves in the same way in the Medicine Lake Highlands series, the Lassen Peak series, the S. California batholith, the Central Nevada series and the Scottish Caledonian series. In each of these the sodium content is nearly, but not quite, constant throughout the whole range, reaching a feeble maximum in the intermediate members of the series. The close approach to a constant value for sodium in all the members of a calc-alkali rock series was long ago remarked upon by BOWEN (1927, p. 100).

The Crater Lake and Lesser Antilles series, characterised by their lower content of potassium, show a different behaviour for sodium. Here, the sodium content shows a small but steady rise throughout. This leads to higher values of Na at the acid end than in the other series.

Potassium, Barium, Rubidium, Caesium, Thallium, Lead (Figs. 13a to 13g)*Potassium*

Although the amounts of potassium in the parental magmas are somewhat variable, the behaviour of this element is the same in all the series except those of Crater Lake and the Lesser Antilles. Potassium increases in amount throughout any given series, the increase being more marked at the acid end. The Crater

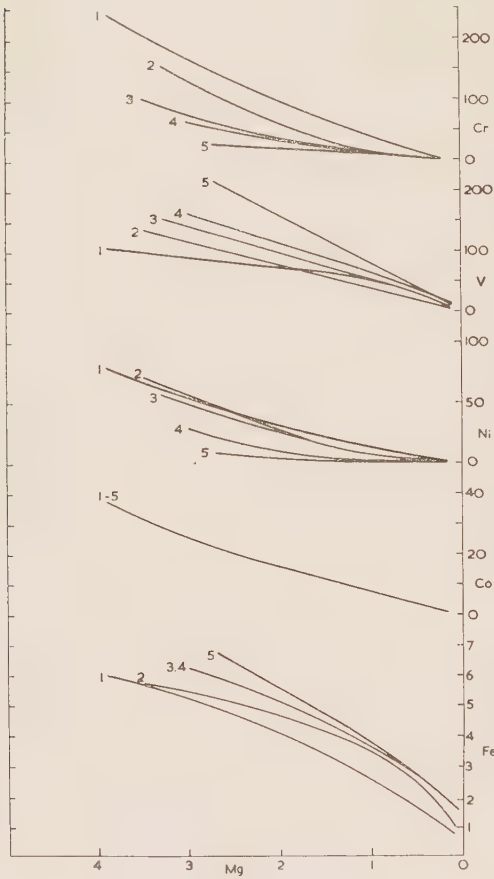


Fig. 11.

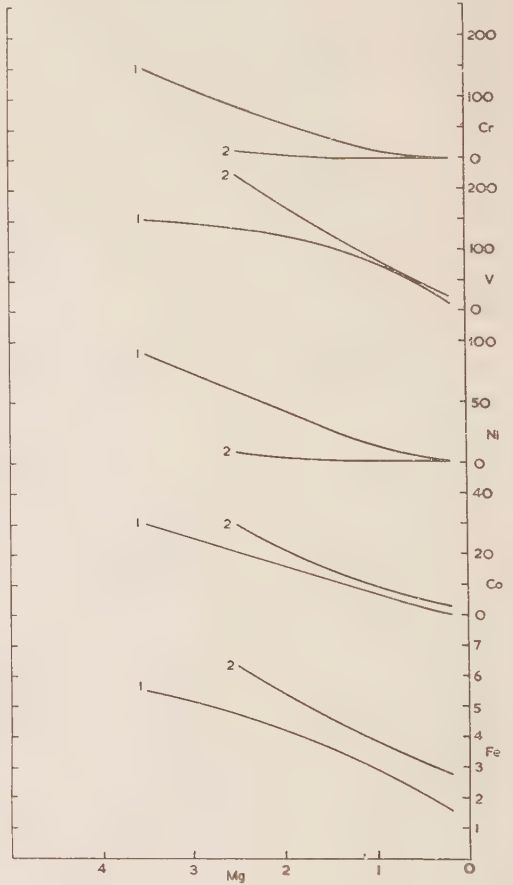


Fig. 12.

Fig. 11. Variation of Cr, V, Ni, Co and Fe with respect to Mg. 1. Scottish Caledonian; 2. Medicine Lake Highlands; 3. Lassen Peak; 4. Southern California Batholith; 5. East Central Sierra Nevada (calc-alkali). Values for trace elements in ppm; values for Mg and Fe in weight percent.

Fig. 12. Variation of Cr, V, Ni, Co and Fe with respect to Mg. 1. Crater Lake; 2. Lesser Antilles. Values for trace elements in ppm; values for Mg and Fe in weight percent.

Lake and Lesser Antilles series both have slightly lower initial amounts of potassium and the amount of potassium shows a steady increase in the Crater Lake series (and in that of the Lesser Antilles as far as it can be traced) with no more marked increase at the acid end of the series. Thus these series remain relatively low in potassium throughout.

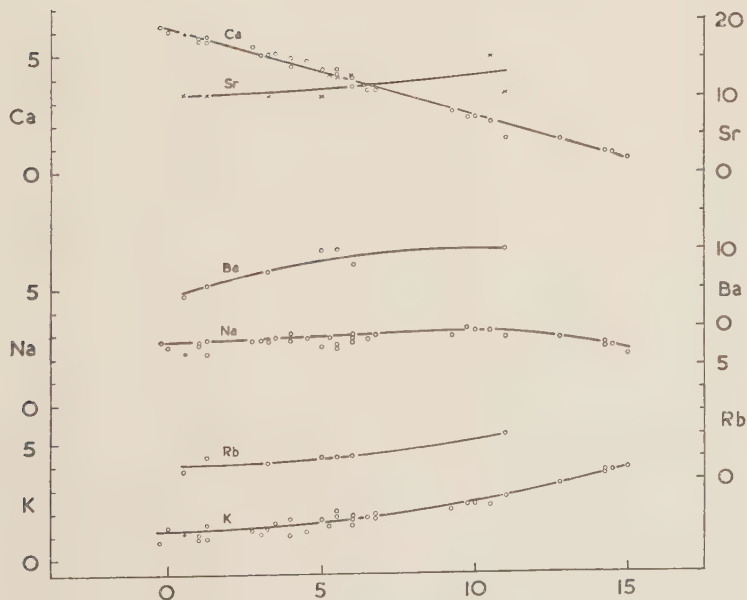
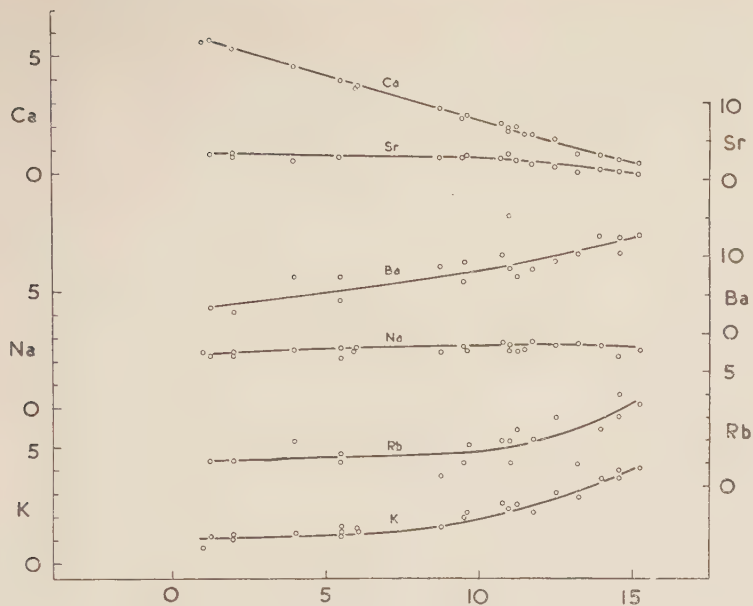


Fig. 13 a-g. Variation in Calcium, Strontium, Barium, Sodium, Rubidium and Potassium. Values in weight percent, Sr, Ba and Rb $\times 100$.

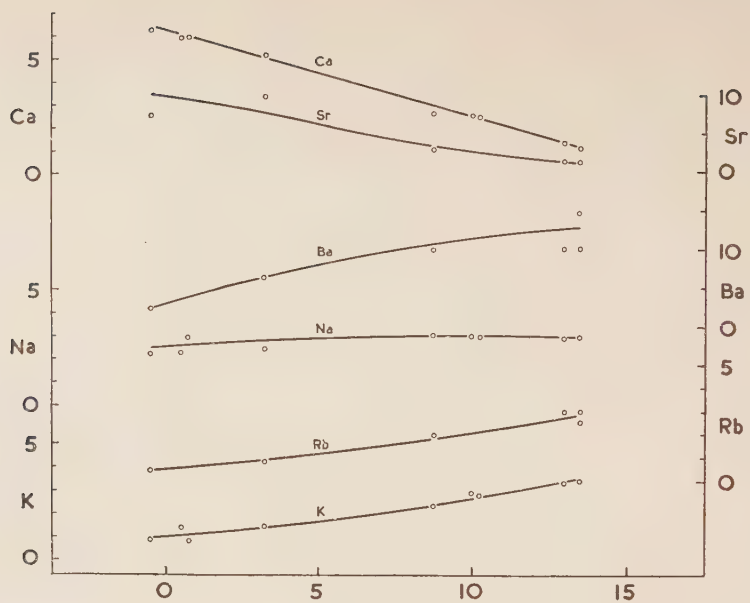


Fig. 13c. Medicine Lake Highlands.

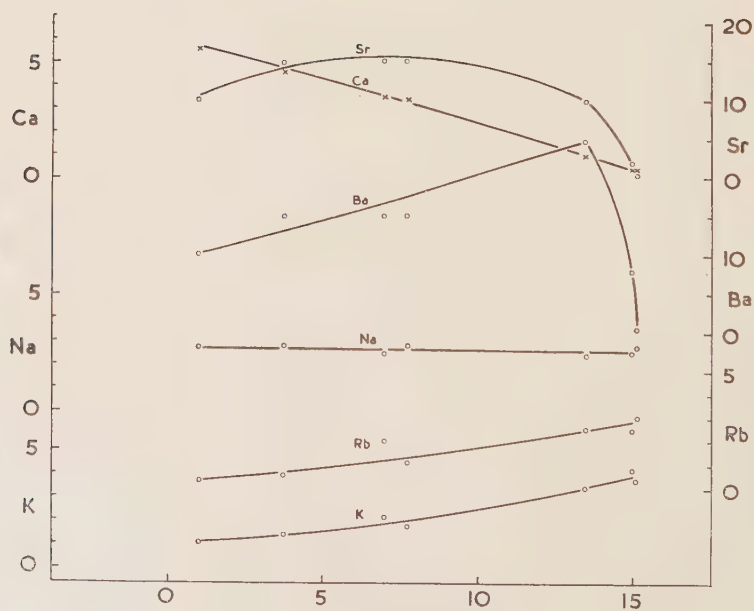


Fig. 13d. E. Central Sierra Nevada.

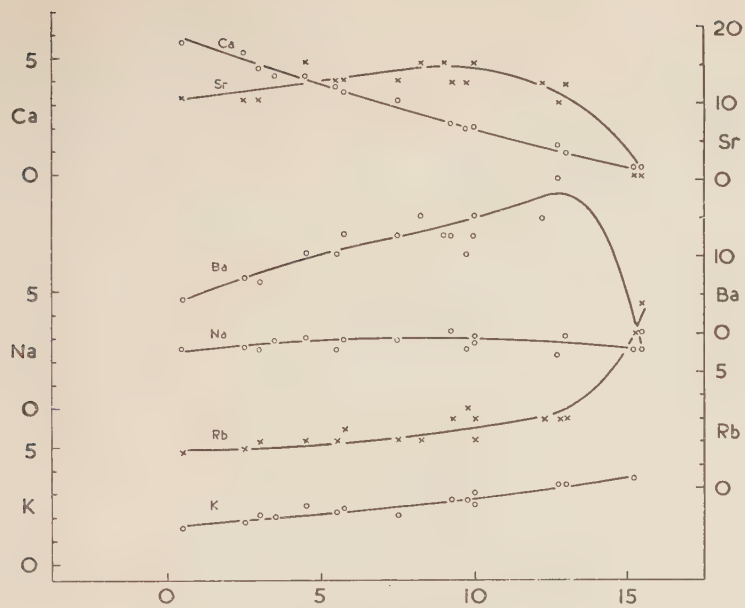


Fig. 13e. Scottish Caledonian

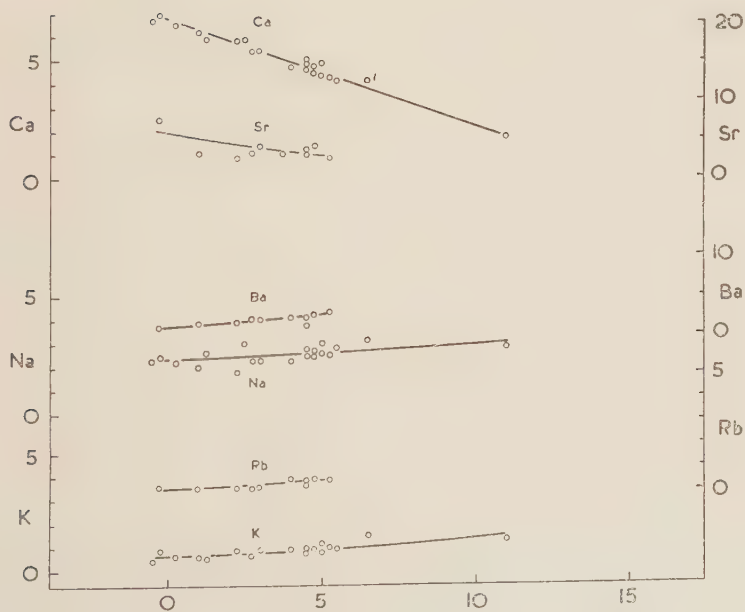


Fig. 13f. Lesser Antilles.

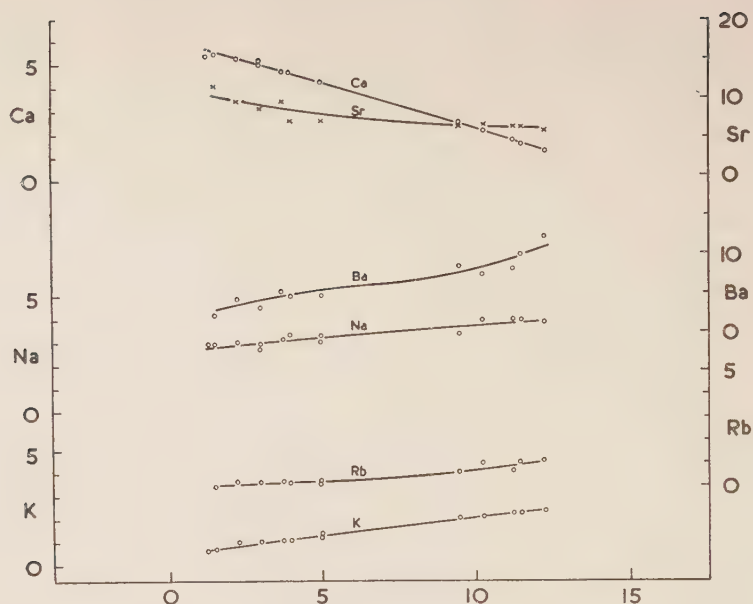


Fig. 13g. Crater Lake.

Barium

The South California batholith, Medicine Lake series, Lassen Peak series and Scottish Caledonian series all have approximately the same initial amounts of Ba, but this element is definitely greater in amount in the E. Central Sierra Nevada series. In all these, Ba rises steadily in amount as the more acid rocks are approached. But in the E. Central Sierra Nevada series, as in the Scottish Caledonian series, there is a sudden drop in the Ba content at the extreme acid end. These two series have more highly differentiated end products than the others and the final residual magma is depleted in Ba. The Lassen Peak series would probably show the same feature, but unfortunately we have not been able to test this.

The Ba/K ratios do not show, in general, a great deal of change in any one series. There is a tendency for a slight rise at the beginning of a series, followed by a period in which the ratio remains more or less constant, and finally the ratio may fall—as in the Lassen Peak series and the Scottish Caledonian series. The E. Central Sierra Nevada series, however, shows a fall in the Ba/K ratio throughout.

The Crater Lake series shows a slow increase in the Ba content, tending to become greater as the more acid rocks are reached, but the Ba/K ratio remains more or less unchanged throughout. The same remarks apply to the Lesser Antilles series, as far as we have traced it.

Rubidium

The most striking feature here is the almost complete parallelism of the curves for Rb and K in all the series, indicating the constancy of the Rb/K ratio. In the early stages of each series, the Rb/K ratio tends to be a little lower than the

average, but it is only at the extreme acid end of the Scottish Caledonian series, representing residual aplites, that there is any appreciable rise in the ratio. Having regard to the ionic radii of the two elements, one would expect the Rb/K ratio to increase in the later rocks, but it is evident that such an increase must be very small and only becomes appreciable at the final residual stage. This constancy of the Rb/K ratio has been observed also by AHRENS, PINSON and KEARNS (1952). But although the ratio is constant in each series its value is not the same in all. The average ratio $Rb \times 100/K$ is 0.84 for the Scottish Caledonian, 0.76 for the Medicine Lake series, 0.59 for Lassen Peak, 0.81 for the Southern California batholith and 0.61 for the East Central Sierra Nevada series. For the two series less rich in potassium, namely Crater Lake and Lesser Antilles, the ratio is definitely lower being 0.28 and 0.36 respectively. These values may be compared with the average ratio of 0.82 for the Skaergaard rocks and with the average ratio 0.9 for all igneous rocks as given by AHRENS, PINSON and KEARNS.

Caesium

In most of the rocks where Cs has been sought it lies below the limits of sensitivity (15 ppm) and it is only at the extreme acid end of certain series (S. California batholith, E. Central Sierra Nevada, Scottish Caledonian) that it can be detected and even then it lies only just above the sensitivity limit.

Thallium

Thallium behaves in the same way as caesium and is normally not found even in the most acid rocks, although the sensitivity limit is much lower (2 ppm). The recent work by SHAW (1952) on the geochemistry of this element has shown that for most rocks the amount present is below our limit of sensitivity and only rises above this for certain granites and rhyolites.

Lead

Lead is present in small amounts (10 to 15 ppm) in the rocks of most of the series and often falls below the limits of sensitivity at the more basic end. It only becomes appreciable in amount at the acid end of the more potassic series where it normally ranges from 30 to 50 ppm. In the less potassic series of Crater Lake it remains low throughout, and this is true of the Lesser Antilles series too, as far as it can be traced.

Boron, Zirconium

Boron

This element has been determined for a number of samples in certain of the rock series, using copper electrodes. The results are difficult to interpret. In the Lassen Peak series, the B content appears to rise as the rocks become more acid. But in the case of the S. California batholith and the Crater Lake series it occurs sporadically throughout and does not seem to be following any particular trend.

On the other hand, the boron content of the Scottish Caledonian series decreases as the rocks become more acid.

Zirconium (Fig. 14)

Zirconium behaves in much the same way in every series, though the amount of Zr present varies from series to series. In general, the Zr content is low at the basic end of each series and then tends to rise, after which it seems more or less constant until the extreme acid end when it tends to fall.

Molybdenum, Tin, Cerium, Germanium, Beryllium and Indium

Molybdenum (sensitivity 2 ppm) was detected only in one altered rock (No. 25, Table 1) from the South California batholith. A noteworthy feature is the absence of appreciable *tin* (sensitivity 5 ppm) in every series even in the most acid rocks. *Cerium* (sensitivity 300 ppm), *germanium* (sensitivity 15 ppm), *beryllium* (sensitivity 5 ppm) and *indium* (sensitivity 1 ppm) were not observed in any of the samples.

SANDELL'S (1952) work on the geochemistry of beryllium shows that basic igneous rocks have, on the average, about 1 ppm and granitic rocks about 3 ppm, values below our limit of sensitivity. Again, SHAW'S (1952) study on the geochemistry of indium indicates that the indium content of our rocks would be below our limit of sensitivity for this element.

THE ACCUMULATIVE ROCKS

Attention has been directed so far to those members of each series which lie on smooth curves on the variation diagram and which are believed to be representative of the liquid line of descent. We have, however, determined the trace element content of a few samples which occur at the basic end of the series, do not lie on the curves, and are believed to be due to a certain amount of crystal accumulation. Five samples come from the S. California batholith (Nos. 1 to 5, Table 1), one from Lassen Peak (No. 1, Table 2), one from Crater Lake (No. 1, Table 7) and one from the Lesser Antilles (No. 1, Table 6).

In general, all these rocks show varying degrees of enrichment in Mg and Ca and sometimes, also, in Fe or Al. They are impoverished in Si, K and Na and, sometimes, in Al. Among the trace elements there is enrichment in Cr, V, Ni, Co and Sc, and impoverishment in Li, Ba, Rb and sometimes Zr. Sr may show enrichment when plagioclase accumulation occurred (i.e. in those rocks enriched in Al) or it may show impoverishment when accumulation of dark minerals took place (i.e. in those rocks impoverished in Al).

Similar results have been obtained already from a study of the accumulative rocks of the Scottish Caledonian series (NOCKOLDS and MITCHELL, 1948) and are, indeed, what would be expected if these rocks represent early liquids enriched to a greater or less extent by the accumulation of early formed crystals of the ferromagnesian minerals and/or early formed plagioclase feldspar.

THE PARENTAL MAGMAS

The approximate chemical compositions of the supposed parental magmas of the various rock series dealt with in this paper are collected together in Table 8, together with one or two other analyses for comparison. They all bear a close resemblance to one another, and the only essential difference between analyses 1 to 6, and analyses 7 to 10 lies in the slightly lower K_2O content of the latter. This difference, although small, is apparently sufficient to account for the difference in the potassium content which is observable throughout the differentiation of the two groups. That this is not the complete explanation is shown by the Santorin lavas which differentiate in the same way as the Crater Lake group. The analysis of the Paricutin lava is of great interest, showing a close relation to the parental magmas of Crater Lake, the High Cascades and the Lesser Antilles but with a lower Fe/Mg ratio.*

Table 8. Approximate chemical composition of parental magmas of some calc-alkali series, with norms and Fe/Mg ratios

	1	2	3	4	5	6	7	8	9	10
SiO ₂	54.4	54.8	52.6	53.5	56.3	54.0	54.0	54.9	53.2	53.4
TiO ₂	1.0	0.9	1.0	0.4	1.1	0.7	1.0	0.8	1.3	1.1
Al ₂ O ₃	16.5	18.5	17.9	18.3	17.3	19.2	17.6	18.1	18.4	19.0
Fe ₂ O ₃	1.6	1.1	3.0	3.2	1.9	2.4	1.7	3.9	2.6	3.2
FeO	6.4	5.9	6.0	5.3	6.3	6.4	6.0	3.8	5.9	5.9
MnO	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
MgO	6.6	5.8	5.9	5.5	4.7	4.5	7.0	5.4	5.3	4.0
CaO	7.8	8.7	8.6	9.0	7.9	7.8	8.1	8.6	8.2	9.3
Na ₂ O	3.5	3.0	3.5	3.4	3.1	3.6	3.6	3.4	3.9	3.1
K ₂ O	1.7	1.0	1.2	1.1	1.2	1.2	0.7	0.8	0.8	0.8
P ₂ O ₅	0.3	0.1	0.2	0.2	0.1	0.2	0.2	0.2	0.3	0.1
qz	0.5	4.4	0.4	2.1	8.1	2.6	1.5	6.9	1.3	5.8
or	10.0	6.1	7.2	6.7	7.2	7.2	3.9	5.0	5.0	5.0
ab	29.3	25.2	29.3	28.8	26.2	30.4	30.4	28.8	33.0	26.2
an	24.5	33.9	29.5	31.1	29.7	32.5	30.0	31.1	30.0	35.3
CaSiO ₃	5.1	3.5	5.2	5.1	3.6	2.2	3.9	4.3	4.1	4.2
MgSiO ₃	16.5	14.5	14.8	13.7	11.7	11.2	17.5	13.5	13.2	10.0
FeSiO ₃	9.1	8.8	6.9	6.6	8.3	8.7	7.9	2.6	6.7	6.5
mt	2.3	1.6	4.4	4.6	2.8	3.5	2.6	5.6	3.7	4.6
il	2.0	1.7	2.0	0.8	2.1	1.4	2.0	1.5	2.4	2.1
ap	0.7	0.3	0.5	0.5	0.3	0.5	0.5	0.5	0.7	0.3
Fe	60	61	66	66	69	71	58	64	67	74
Mg	40	39	34	34	31	29	42	36	33	26

1. Scottish Caledonian. Average of four analyses of pyroxene-mica diorite, NICKOLDS (1941), A, of Table 4.

2. Medicine Lake Highlands. Basalt inclusion in recent dacite of Glass Mountain, ANDERSON (1941), Anal. 3, p. 390.

3. Santorin. Basic inclusion in Ktenas lava-flow. GEORGALAS and PAPASTAMATIOU (1951), Anal. 4, p. 36.

4. Lassen Peak region. Average of two analyses (basalts, Shasta County. CLARKE (1915), Anal. N and O, p. 175.)

5. S. California batholith. Average of three analyses (quartz-biotite norites, LARSEN (1948), Anal. 8 and 9, p. 50, and "Bonsall tonalite," LARSEN (1948), Anal. 2, p. 66).

6. East Central Sierra Nevada. Pyroxene andesite intrusion (CURTIS, No. 9-28-45).

7. Paricutin, Mexico, eruption of 1944. (Unpublished analysis by J. H. SCOON, recalculated on a water-free basis.)

8. Crater Lake. Olivine basalt, N. base of Union Peak, WILLIAMS (1942), Anal. 4, p. 148.

9. High Cascades lavas. Average of two analyses (Basalt of Minto type, THAYER (1937), p. 1628 and micro-norite related to Minto basalt, THAYER (1937), p. 1628).

10. Lesser Antilles. Average of three analyses (basalt, S. Soufriere Hill, Montserrat MacGREGOR (1938), "labradorite z." St. Kitt's LYEROIX (1924), "dacitoid," basaltic type, Old Souma. Soufriere, St. Vincent, LACROIX (1924), p. 403).

* It is somewhat richer in Mg than the analyses listed by WILLIAMS (1950).

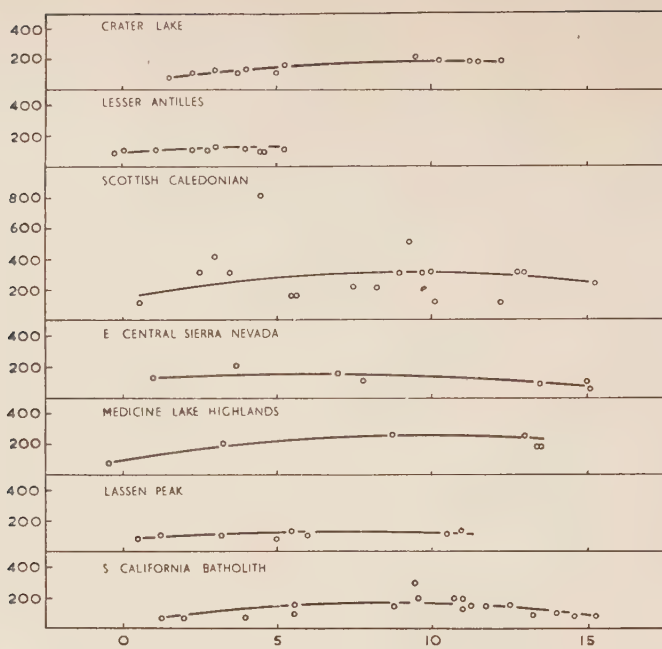


Fig. 14. Variation in Zirconium. Values in ppm.

Table 9. Content of certain trace elements in parental magmas

	1	2	3	4	5	6	7	8
Si ⁺⁴	254·10 ³	256·10 ³	250·10 ³	263·10 ³	252·10 ³	252·10 ³	256·10 ³	249·10 ³
Al ⁺³	87·10 ³	98·10 ³	97·10 ³	92·10 ³	102·10 ³	93·10 ³	96·10 ³	101·10 ³
Ti ⁺⁴	6·10 ³	5·10 ³	3·10 ³	7·10 ³	4·10 ³	6·10 ³	5·10 ³	7·10 ³
Fe ⁺³	11·10 ³	8·10 ³	23·10 ³	13·10 ³	17·10 ³	12·10 ³	27·10 ³	22·10 ³
Mg ⁺²	40·10 ³	35·10 ³	33·10 ³	28·10 ³	27·10 ³	42·10 ³	32·10 ³	24·10 ³
Fe ⁺²	50·10 ³	46·10 ³	42·10 ³	49·10 ³	50·10 ³	47·10 ³	29·10 ³	46·10 ³
Na ⁺¹	26·10 ³	22·10 ³	25·10 ³	23·10 ³	27·10 ³	27·10 ³	25·10 ³	23·10 ³
Ca ⁺²	56·10 ³	62·10 ³	64·10 ³	56·10 ³	56·10 ³	58·10 ³	61·10 ³	66·10 ³
K ⁺¹	14·10 ³	8·10 ³	9·10 ³	10·10 ³	10·10 ³	6·10 ³	7·10 ³	7·10 ³
Ga ⁺³	15	20	(20)	30	30	20	(25)	25
Cr ⁺³	220	100	(150)	60	20	250	(150)	15
V ⁺³	100	100	(150)	150	200	150	(150)	225
Li ⁺¹	25	50	(25)	25	20	15	(15)	20
Ni ⁺²	80	70	(60)	30	10	150	(85)	5
Co ⁺²	40	25	(30)	20	20	45	(30)	30
Y ⁺³	*	*	(20)	20	20	*	(15)	20
Sr ⁺²	1000	750	(1000)	275	1000	800	(1100)	750
Ba ⁺²	400	250	(300)	250	1000	150	(150)	100
Rb ⁺¹	100	50	(50)	100	50	*	(*)	20
Fe	60	61	66	69	71	58	64	74
Mg	40	39	34	31	29	42	36	26

1. Scottish Caledonian.
 2. Medicine Lake Highlands.
 3. Lassen Peak region (trace elements extrapolated from variation diagrams).
 4. S. California batholith.

5. E. Central Sierra Nevada.
 6. Paricutin.
 7. Crater Lake (trace elements extrapolated from variation diagrams).
 8. Lesser Antilles.

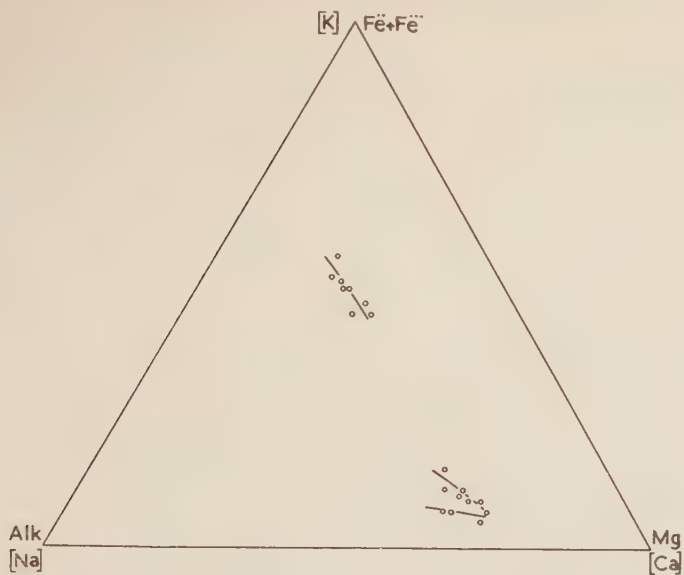


Fig. 15. Diagram showing variation in composition of parental magmas.

It will be noticed that, in both groups of analyses, there is some variation in the ratio of total iron to magnesium and, indeed, the analyses are found to lie on a smooth curve when plotted to show the variation between magnesium, total iron, and total alkalis (Fig. 15). As already mentioned, when considering the trace elements concerned, the content of Cr, V, Ni and Co is closely related to the Fe/Mg ratio (Table 9). Yttrium, too, falls below the limit of sensitivity in the more magnesian parental magmas but occurs in small amounts in the more ferri-ferous ones. Strontium varies little, except in the case of the parental magma of the Southern Californian batholith, where it is unduly low. Rubidium more or less follows potassium, but the barium content is variable in the first group of analyses, though nearly constant in the second.

Acknowledgments—We wish to express our gratitude to Prof. E. S. LARSEN, Prof. H. WILLIAMS, Prof. J. ORCEL, Dr. C. A. ANDERSON, Mr. J. H. HALSEY, Mr. G. H. CURTIS, Mr. D. B. SLEMMONS, Dr. A. G. MACGREGOR, Dr. W. F. FOSHAG and for providing us with samples of rocks which had already been analysed for their major constituents.

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Precision and accuracy of chemical analysis of silicate rocks

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ABSTRACT

Replicate analyses by 35 laboratories of a granite and a diabase, especially prepared as standards, give means and standard deviations which should be invaluable for calibration purposes in spectrochemical and chemical laboratories. It is clearly shown that relative error varies inversely with concentration of the constituent (e.g. 0.1% for SiO_2 , 10% for P_2O_5).

A test of accuracy has also been made by 11 laboratories, each analyzing a synthetic glass of the proportions found in granite. The composition of the glass is known within $\pm 0.02\%$ for SiO_2 , $\pm 0.01\%$ for Al_2O_3 and is without significant error for the remaining constituents. The means computed from the chemical analyses showed satisfactory agreement for MgO , CaO , Na_2O , K_2O ($< 0.1\%$). For SiO_2 and Al_2O_3 a reciprocal systematic error appeared whereby SiO_2 was 0.4% low and Al_2O_3 was 0.6% high; total SiO_2 and Al_2O_3 agreed almost exactly ($< 0.1\%$) with the glass standard.

As a result of these tests attention is directed anew to the practical but complex problem of evaluating error in a *single* analysis made by conventional methods. The advantages for many purposes of the more rapid photometric and spectrochemical methods and (for many igneous rocks) of micrometric methods are outlined.

INTRODUCTION

In three recent publications (FAIRBAIRN *et al.*, 1951; SCHLECHT, 1951; FAIRBAIRN and SCHAIRER, 1952) the matter of precision and accuracy of chemical analysis of silicate rocks has received some long overdue attention. The investigation had its immediate origin in the need for reliable standards in spectrochemical analyses of major elements in silicate rocks; the data obtained, however, provide fuel for fruitful discussion in the field of analytical chemistry alone. It is the purpose of this paper to summarize and discuss certain of the results of the three publications listed above. Some additional analyses are now available* and are included in the compilation.

THE STANDARDS

A granite (G-1) from Westerly, Rhode Island, and a diabase (W-1) from Centreville, Virginia, provided source material for the preparation of the rock standards. Details of preparation are given elsewhere (FAIRBAIRN *et al.*, 1951; pp. 1-6) and need not be repeated here. It is sufficient to state that the requirement of a homogeneous product has been met. Samples of these standards have been analyzed by chemists in 35 laboratories† throughout the world, providing highly significant data on precision.

A synthetic glass of granite composition, prepared by J. F. SCHAIRER at the Geophysical Laboratory, Washington, served as a standard to test accuracy of analysis. It was analyzed by chemists from 12 laboratories, 11 of which had

* These were obtained through the courtesy of Dr. MICHAEL FLEISCHER, Geological Survey, Washington, D.C.

† As of February, 1952.

previously analyzed G-1 and W-1. Its preparation, tolerances, in composition, and degree of homogeneity have been described in detail (FAIRBAIRN and SCHAIRER, 1952). Unlike G-1 and W-1*, the synthetic glass is no longer available for analysis, as only 92 g were prepared.

PRECISION OF ANALYSIS

Precision, or reproducibility, of analysis can be considered under three heads (1) Precision of replicate analyses by the *same* analyst working in a given laboratory and using the same procedures for each analysis. The precision obtained should be of a high order if the analyst is experienced. (2) Precision of replicate analyses by different *analysts* working in a given laboratory and using the same procedures for each analysis. With experienced analysts the order of precision should be fairly high under these conditions. (3) Precision of replicate analyses by different analysts working in *different* laboratories and using a variety of procedures. The order of precision under these inter-laboratory conditions is distinctly lower than in the first two cases.

The two rock standards G-1 and W-1 furnished data on all three above groupings, but major interest lies in the inter-laboratory test of precision. Since the 35 co-operating laboratories include government, university, and industrial analysts from representative countries, the data are believed to reflect the current state of silicate analysis.

Results of the computations on precision are compiled in Table 1. Since the correct analyses can never be known, the arithmetic mean for each constituent is the best estimate available† and affords a basis for estimating precision.

The remaining statistical data in the table represent standard computations as there noted. For those unfamiliar with the meaning of standard deviation and error, the following will be helpful. In Table 1 the standard deviation of 0.35 for SiO_2 in G-1 means that, in a *single* analysis of this type of rock, it is improbable that more than 1 in 3 would exceed $72.36 + 0.35$, or be less than $72.36 - 0.35$. Similarly for Fe_2O_3 in G-1 (where $s = 0.34$), it is improbable that more than 1 in 3 would exceed $0.93 + 0.34$, or be smaller than $0.93 - 0.34$. Percentage-wise, however, the relative deviation for SiO_2 is only 0.5%, whereas for Fe_2O_3 it is 37%.

The standard errors of 0.07 for SiO_2 and 0.06 for Fe_2O_3 express a 2 : 3 probability that the mean of 72.36 for SiO_2 is correct to ± 0.07 and that for Fe_2O_3 is correct to ± 0.06 . Percentage-wise, this may be expressed for SiO_2 as an error of 0.1% and for Fe_2O_3 as 7%. These are estimates, since the arithmetic mean is itself an estimate, but are nevertheless significant.

Histograms showing the range of individual determinations have been

* These two rock standards are available in small quantities to responsible persons working in silicate chemistry. Inquiries should be directed to Dr. MICHAEL FLEISCHER, U.S. Geological Survey, Department of the Interior, Washington, D.C.

† The point of view followed by SCHLECHT (1951), that computation of arithmetic means is not warranted, is in my opinion unrealistic. Any measurement is an estimate of an unattainable true value, and as long as data derived from such estimates are recognized themselves as estimates, much can be learned without loss of perspective.

published elsewhere (FAIRBAIRN *et al.*, 1951, p. 33; SCHLECHT, 1951)*. These show very clearly a large scatter for certain constituents, notable Al_2O_3 , Fe_2O_3 , and H_2O^+ in both standards; K_2O in the diabase, and MgO in the granite. In part this scatter is to be expected if the concentration of a constituent is extremely low, as the following section shows.

If arithmetic means for each constituent in each standard are plotted against relative deviations, as in Fig. 1, it becomes evident that in general the latter vary inversely with the concentrations of each constituent†. Lines have been drawn

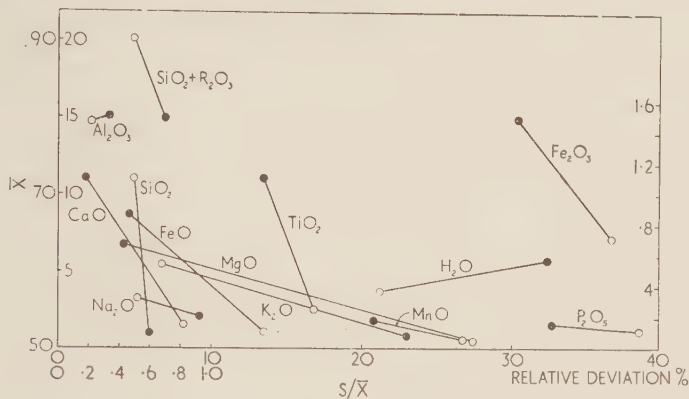


Fig. 1

between G-1 and W-1 values to accentuate this relation. All have NW-SE trends except Al_2O_3 and H_2O . Thus an analyst's determination of MgO at the concentration found in diabase is likely to be much more reliable than a determination of the much smaller amount found in granite. This has been obvious to most analysts for a long time, but apparently needs emphasis where the geologic fraternity is concerned. Depending on the use being made of a silicate analysis, the uncertainty in any constituent, represented by the standard deviation, may or may not be critical. In any case it is important to be aware of its order of magnitude, and this the present investigation provides insofar as silicate rocks are concerned.

ACCURACY OF ANALYSIS

The preceding section on precision says nothing regarding accuracy and no direct approach is possible from the standards G-1 and W-1. The source of present information on accuracy of analysis is the synthetic glass of granite composition referred to on page 143. This glass was analyzed by 11 of the laboratories whose previous work on G-1 and W-1 was closest to the arithmetic mean for each constituent. Although more analyses would have been desirable, the test was limited by the small quantity of glass standard available.

* Table 1 includes a number of analyses not available for these histograms, but the range of values remains essentially the same.

† Since submitting the manuscript my colleague L. H. AHRENS has pointed out that a more elegant demonstration of this inverse relationship is obtained if the data are plotted on log-log paper.

Table 1. *Revised Statistical Data on Standard Rocks*

	Means and Errors etc.	G-1 Granite (Westerly, R.I.)	W-1 Diabase (Centreville, Va.)
SiO ₂	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	72.36* → 72.86 0.1243 0.35 0.5 29 0.07 0.1	52.34* → 52.69 0.1006 0.32 0.6 32 0.06 0.1
TiO ₂	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	0.25 0.001773 0.04 17 29 0.01 3.1	1.10 0.02149 0.15 14 31 0.03 2.4
Al ₂ O ₃	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	14.44† → 13.94 0.0995 0.32 2.2 28 0.06 0.4	15.07† → 14.72 0.2482 0.50 3.3 32 0.09 0.6
Fe ₂ O ₃	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	0.93 0.1167 0.34 37 28 0.06 7	1.50 0.2079 0.46 30 30 0.08 5.5
FeO	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	0.99 0.01787 0.13 13.5 29 0.02 2.5	8.71 0.1708 0.41 4.7 31 0.07 0.9
MnO	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	0.027 0.0000538 0.007 28 27 0.001 5.2	0.165 0.00118 0.034 21 32 0.006 3.7
MgO	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	0.39 0.01096 0.10 27 28 0.02 5.1	6.63 0.07654 0.28 4.2 32 0.05 0.7
CaO	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	1.41 0.01334 0.11 8.2 29 0.02 1.5	10.96 0.03715 0.19 1.8 33 0.03 0.3
Na ₂ O	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	3.25 0.02825 0.17 5.2 28 0.03 1.0	2.00 0.03416 0.19 9.3 32 0.03 1.6
K ₂ O	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	5.42 0.1371 0.37 6.8 28 0.07 1.3	0.63 0.02111 0.15 23 32 0.03 4.1
H ₂ O+	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	0.365 0.00598 0.08 21 28 0.015 4	0.56 0.03272 0.18 32 31 0.03 5.7
P ₂ O ₅	$\bar{x}$ s^2 s C n $s_{\bar{x}}$ E	0.09 0.00121 0.03 39 27 0.01 7.5	0.126 0.0017 0.04 33 30 0.01 6

Table 1 (continued)

	Means and Errors etc.			G-1 Granite (Westerly, R.I.)			W-1 Diabase (Centreville, Va.)		
	$\bar{x}$	s^2	n	s	$s\bar{x}$	E			
R ₂ O ₃									
	$\bar{x}$								
	s^2								
	n								
R ₂ O ₃ + SiO ₂									
	$\bar{x}$								
	s^2								
	n								
Totals									

Explanation of Symbols

 $\bar{x}$ = arithmetic mean s^2 (variance) = $\frac{\sum d^2}{n-1}$, where d = deviation from the mean of single measurements n = number of measurements $s = \sqrt{s^2}$ = standard deviation (of a single measurement) $s\bar{x} = \frac{s}{\sqrt{n}}$ = standard error (of the mean) $C = \frac{s}{\bar{x}}\%$ = relative deviation (coefficient of variation) $E = \frac{s\bar{x}}{\bar{x}}\%$ = relative error

* Preferred Estimate 0.5% higher for G-1; 0.35% higher for W-1.

† Preferred Estimate 0.5% lower for G-1; 0.35% lower for W-1.

The composition decided on for the glass was as follows:

Norm		Weight %	
Q	27.0	SiO ₂	72.64
Cor	1.0	Al ₂ O ₃	15.78
Or	34.0	CaO	1.82
Ab	27.0	MgO	0.80
An	9.0	K ₂ O	5.76
En	2.0	Na ₂ O	3.19
	100.0		99.99

Iron, unfortunately, had to be omitted in order to avoid uncertainty in the final composition. Impurities found in the glass after its preparation were 0.15% Fe₂O₃, 0.08% H₂O+, 0.10% Pt. These were to be expected because of the use of steel mortars, platinum crucibles, and water adsorption by the finely ground glass powder. For the major constituents, deficiencies of 0.02% for SiO₂ and of 0.01%

for Al_2O_3 are the only significant uncertainties in the composition (FAIRBAIRN and SCHAIRER, 1952).

Table 2 compares the analytical work on the glass with the known composition. The order of magnitude of precision (s , s_f , C , E) is seen to be the same as that computed for G-1 (Table 1), even though the number of analyses is considerably less.

Comparison of the means $\bar{x}$ with the standard values shows differences of somewhat less than 0.1% for MgO , CaO , Na_2O and K_2O . This order of agreement is considered to be satisfactory. For SiO_2 and Al_2O_3 , however, a systematic discrepancy of low SiO_2 (0.4%) and high Al_2O_3 (0.6%) is in evidence. It is not fortuitous that these discrepancies are of opposite sign and of the same order of magnitude, since the table shows that the total of SiO_2 and Al_2O_3 is identical* with the standard. It is well known of course that it is difficult to isolate all the SiO_2 in standard analytical procedures and that the unrecovered portion remains with Al_2O_3 , but this is the first quantitative investigation of the problem where a proper standard was available.

This SiO_2 – Al_2O_3 discrepancy is not of a magnitude which is critical for many geological investigations, but it is more than a little annoying to conscientious analysts. Special precautions may be taken in some cases to insure recovery of SiO_2 ; this was done by Laboratory 12† with notable success, but may not be possible with certain silicate mixtures. Spectrochemical study of the R_2O_3 precipitates should shed some light on the problem, but no data are as yet available.

An additional refinement is disclosed by statistical means. If values for each constituent which differ from the mean by more than $2s$ are discarded‡, it is found that the revised means for Na_2O , CaO , K_2O (MgO excepted) change in the direction of the standard value; the new mean for SiO_2 alters the difference from the standard from 0.4 to 0.5 and for Al_2O_3 from 0.6 to 0.5. These shifts, and especially the SiO_2 – Al_2O_3 change, confirm the standard composition.

BEARING OF ACCURACY TEST ON G-1 AND W-1 MEANS

The satisfactory agreement of means obtained in the accuracy test with the glass standard provides circumstantial evidence that the averages computed for MgO , CaO , Na_2O , and K_2O in G-1 and W-1 are probably very close to the true values. For SiO_2 it seems reasonable to assume for the present that the G-1 value is 0.5% too low and the W-1 value is 0.35% too low (lower SiO_2 content). Histograms for SiO_2 and $\text{SiO}_2 + \text{R}_2\text{O}_3$ offer qualitative confirmatory evidence for these corrections (Fig. 2). Frequency is plotted against weight percent. In each standard the SiO_2 histogram is highly asymmetric, whereas the $\text{SiO}_2 + \text{R}_2\text{O}_3$ plots are in complete contrast. That is, experimental error alone could account for the essentially symmetrical dispersion shown by $\text{SiO}_2 + \text{R}_2\text{O}_3$; for SiO_2 , on the

* This identity of numbers as such is not significant, for the SiO_2 and Al_2O_3 in the standard have errors of 0.02 and 0.01 respectively (see above). Even with these errors included, however, agreement with the $\text{SiO}_2 + \text{Al}_2\text{O}_3$ mean is phenomenally close.

† Since this laboratory did not take part in the original investigation of G-1 and W-1, its results with the glass are not included in the means in Table 2.

‡ A commonly used statistical device, indicating the probability that more than experimental error is involved in such high or low values.

other hand, more than experimental error is involved. This confirms qualitatively for G-1 and W-1 the quantitative conclusions shown for the glass standard. The preferred values for SiO_2 are indicated in Table 1 by arrows.

Current analytical experience indicates that unrecovered SiO_2 will be found with Al_2O_3 . Histograms for G-1 and W-1 should therefore show a reversal of the asymmetry noted for SiO_2 in Fig. 2. This statistical feature is not in evidence,

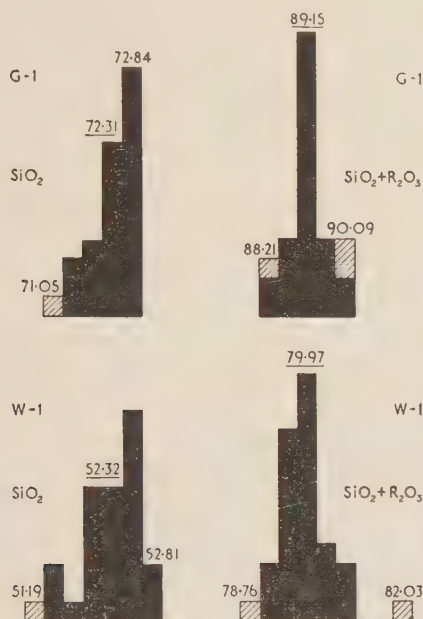


Fig. 2

however, probably because Al_2O_3 is determined by difference—i.e., $\text{Al}_2\text{O}_3 = \text{R}_2\text{O}_3 - (\text{total Fe} + \text{P}_2\text{O}_5 + \text{TiO}_2)$. The analytical discrepancies in the subtracted constituents could easily mask in the histograms the predicted effect of unrecovered SiO_2 . In absence therefore of positive evidence, the means for Al_2O_3 in G-1 and W-1 are diminished in Table 1 by 0.5% and 0.35%, respectively.

For the remaining constituents in G-1 and W-1 (FeO , Fe_2O_3 , TiO_2 , MnO , H_2O^+ , P_2O_5) no confirmation of degree of accuracy is available from the glass standard. For the present, therefore, one can only extrapolate the assumption that, since current procedures for alkalis, lime and magnesia give reasonably accurate results, the same holds true of the procedures used for the untested constituents.

THE PROBLEM OF THE SINGLE ANALYSIS BY STANDARD METHODS

There are available today thousands of chemical analyses of silicate rocks, their number is constantly growing, and the rate of accumulation shows no sign of abatement. Although it is recognized that many of the earlier ones are inferior, there remain nevertheless an impressive number of "superior" analyses which

are in constant use. Until the present investigation was carried out, no large-scale interlaboratory check on precision had ever been made, and no adequate accuracy test of any kind. These tests, summarized in the preceding pages, are an indication of the current status of silicate analysis and, in terms of the averages for each constituent, provide reasonably satisfactory estimates of the composition of the two standards G-1 and W-1. These standards are therefore invaluable in spectrochemical analyses of major elements and for checking purposes in chemical laboratories. Since the estimates of composition were obtained, however, by the prohibitively expensive and time-consuming method of many *replicate* analyses in different laboratories, we are still for practical purposes faced with the matter of evaluating precision and accuracy in a *single* analysis. This is the problem to be met in making use of the so-called "superior" analyses in the literature or in interpreting new ones*.

The material used for analysis may be considered under two heads—single minerals, or mineral aggregates (rocks, soils, etc.). In the former case let us assume a sample of an unaltered mineral from which all impurities have been removed, so that the analysis can be recalculated in terms of a single silicate phase. Since the structure of silicates imposes definite compositional limits, glaring analytical errors are obvious in most cases. However, since substitution of cations in varying degree is almost universal, certain analytical errors may still go undetected as long as the recalculation gives a reasonable formula.

With polyphase material no primary compositional control is available and summation of the analysis between limits 99.75–100.50 is too often regarded by non-chemists as the ultimate goal for satisfactory precision and accuracy. That this is a necessary, but insufficient, criterion, the present investigation shows clearly. Assuming analytical procedures to be reliable, the standard deviations (Table 1) for each constituent in G-1 and W-1 can be used as a guide to precision in future work but, since each represents only a 2 : 3 probability, a 1 : 3 probability still remains that the error in a given analysis is greater than the standard deviation. The reality of this matter was shown in an earlier publication (FAIRBAIRN *et al.*, 1951, pp. 43–44). It seems to be true also that the same analyst may vary considerably in the quality of his determination of a given constituent. For example, in Table 2 the alkali determinations by Laboratory 1 differ from the means established in the test by more than 2s, although alkalis done by the same analyst in G-1 and W-1 were in close agreement with the means. The same is true of all the starred values in Table 2.

The $\text{SiO}_2\text{--Al}_2\text{O}_3$ problem is particularly difficult to evaluate since here a systematic analytical factor is imposed on the normal experimental error. The remedy indicated in Table 1 of adding 0.5% to the SiO_2 average and of subtracting a like amount from the Al_2O_3 average applies only where such means can be computed. The bias of a *single* analysis cannot be satisfactorily estimated. All that can be said is that SiO_2 is likely to be reported as less than the true value and Al_2O_3 as higher.

* No discussion is included here of the quite different matter of *sampling error* in selecting material for analysis.

Table 2. Data on synthetic granite glass
recalculated for comparison with the standard composition

Laboratory	SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	SiO ₂ - Al ₂ O ₃	Total
1	72.30	16.20	0.88	2.05	3.82*	5.40*	88.50	100.65
2	72.40	15.85	0.87	1.84	3.35	5.72	88.25	100.03
3	72.01	16.78*	0.75*	1.92	3.15	5.76	88.79	100.37
4	72.37	16.39	0.90	1.67	3.25	5.57	88.76	100.15
5	72.42	16.12	0.82	1.89	3.08	5.70	88.54	100.03
6	72.75	16.12	0.81	1.85	3.13	5.65	88.87	100.31
7	72.25	16.27	0.82	1.99	3.07	5.76	88.52	100.16
8	72.24	16.34	0.88	2.00	3.11	5.62	88.58	100.19
9	72.11	15.91	0.89	2.35*	3.27	5.75	88.02	100.28
10	72.35	15.98	0.86	1.90	3.27	5.79	88.33	100.15
11	71.38*	16.14	0.86	1.90	3.14	5.84	87.52	99.26
$\bar{x}$	72.23	16.19	0.85	1.94	3.24	5.69	88.42	100.15
$s_{\bar{x}}$	0.10	0.08	0.01	0.05	0.06	0.04	0.11	0.09
E	0.1	0.5	1.6	2.6	2.0	0.7	0.1	0.9
s	0.34	0.26	0.05	0.17	0.21	0.12	0.36	0.31
C	0.5	1.6	5.4	8.7	6.5	2.2	0.4	0.3
12	72.69	15.64	0.84	1.79	3.23	5.61	88.33	99.80
(not in-	72.75	15.75	0.88	1.81	3.05	5.64	88.50	99.88
cluded in	72.51	15.97	0.87	1.85	3.16	5.66	88.48	100.02
above								
average)								
Mean for	72.65	15.79	0.86	1.82	3.15	5.64	88.44	99.91
Lab. 12								
Standard composition	72.64	15.78	0.80	1.82	3.19	5.76	88.42	99.99

Symbols— $\bar{x}$ = arith. mean
 s = standard deviation
 C = % relative deviation
 $s_{\bar{x}}$ = standard error
 E = % relative error
 * = Values which differ from the mean $\bar{x}$
 by more than 2s

Analyses based on
 Fe₂O₃ = 0.15
 H₂O+ = 0.08
 Pt = 0.10
 as the best estimate of un-
 avoidable impurities.
 Each analysis recalculated in
 terms of SiO₂, Al₂O₃, MgO,
 CaO, Na₂O, K₂O only.

In a few fortunate laboratories employing a number of analysts, it is possible to repeat analyses and so provide checks. Partial data of this kind are available for G-1 and W-1. In Table 3 SiO₂, R₂O₃, R₂O₃ + SiO₂ are compared using replicate analyses from two laboratories and the means of the 35-laboratory test. Laboratories A and B show higher SiO₂ values, and lower R₂O₃ values, than the corresponding 35-laboratory means. Nevertheless, total SiO₂ + R₂O₃ is about equivalent for each laboratory. Although the SiO₂ values of Laboratory A and Laboratory B are higher and presumably more accurate than the 35-laboratory

Table 3. Comparison of data on SiO_2 , R_2O_3 , and $\text{SiO}_2 + \text{R}_2\text{O}_3$

	G-1			W-1		
	Lab. A (7 anal.)	Lab. B (5 anal.)	35 laboratories	Lab. A (6 anal.)	Lab. B (5 anal.)	35 laboratories
SiO_2	72.64	72.72	72.36	52.66	52.64	52.34
R_2O_3	16.52	16.55	16.84	27.37	27.45	27.60
$\text{SiO}_2 + \text{R}_2\text{O}_3$ }	89.16	89.27	89.21	80.03	80.09	79.94

means, the bias of a *single* analysis (not an average) from either of these laboratories is still unknown and can only be estimated.

This overall picture of precision of single analyses of silicate rocks by conventional methods is therefore somewhat discouraging. It is scarcely practicable to test every R_2O_3 precipitate by quantitative spectrography for unrecovered SiO_2 , and if chemical methods alone are used much, much research might be required to develop special techniques applicable to various silicate mineral mixtures. For other constituents the probable experimental error of an analysis (if procedural difficulties are eliminated) may, of course, be negligible for the job at hand and if so the matter is simplified. Probably the best that can be done at present is (1) to assume the means for G-1 and W-1 to be close estimates of the true composition and (2) for each analyst to make frequent checks against these standard values. If a control of this kind is not carried out, the immense labour of analyses by conventional methods will too often produce inadequate results, as the present study so abundantly shows.

ALTERNATIVE METHODS

Since conventional methods of silicate analysis are time-consuming at best and the usual single analysis is open to many criticisms, a résumé of alternate procedures will now be presented. These include photometric, spectrochemical, and micrometric methods of analysis.

Photometric Methods

Within the last decade photometric methods of analysis have been developed which can be applied to all major constituents of silicate rocks. Preliminary results have been reported by SHAPIRO and BRANNOCK (1952) and further work is in progress. This type of analysis can be made in about one-fifth the time required for a conventional analysis, requires less experienced personnel, and involves fewer laboratory operations. Summation to $< \pm 1\%$ for a single analysis is normal and can be improved by making replicate runs. Precision is easily controlled and the standards G-1 and W-1 can serve as a reasonable check on accuracy. Although not yet tested, the $\text{SiO}_2\text{-Al}_2\text{O}_3$ problem previously discussed should disappear where photometric methods are used. Furthermore, since

many geological problems do not require high analytical precision, these rapid procedures should be, and are, highly useful. As soon as possible an interlaboratory calibration program should be set up so as to avoid the unhappy situation which now plagues conventional analysis.

Spectrochemical Methods

Although the spectrograph has traditionally been used in geologic work only for minor element determinations, its adaptation to major element analysis offers no unusual problems. Given adequate standards, such as G-1 and W-1, all the major constituents except FeO, H₂O+, P₂O₅ can be determined* (FAIRBAIRN *et al.*, 1951; pp. 25-32). The following advantages are offered by spectrochemical analysis.

(1) The labour and cost per analysis are considerably less than for conventional methods.

(2) Precision is comparable with chemical methods and can be easily improved by replicate runs. Its magnitude is not dependent on the concentration of the constituent.

(3) The spectrum yields a permanent record of the analysis, with (usually) several elements (both major and minor) on the same plate.

(4) Only a few milligrams of sample are required, which in analysis of single minerals may be a critical matter.

Summation to 100 has not yet been thoroughly tested, but the combined chemical (FeO, H₂O, P₂O₅) and spectrochemical (remaining major constituents) results have in several instances given $100 \pm 1\%$. In any case, to be aware of the magnitude of the uncertainty in an analysis is a realistic attitude vastly preferable to blind faith in determinations reported to two decimals and adding to 100.

Micrometric Methods

If a rock fabric shows little or no dimensional orientation of the grains, and the grain size is not too small, micrometric analysis of thin sections is an invaluable ally, especially of the igneous petrologist. Since G-1 and W-1 could be studied to advantage by means of this technique, some interesting data have been obtained (CHAYES in FAIRBAIRN *et al.*, 1950; pp. 59-68). In a comparison of the precision obtained by micrometric analysis on the standard rocks with that of norms calculated from their chemical analyses CHAYES has shown that the former is much superior; in addition, micrometric analysis demonstrates a high degree of homogeneity of the test rock. The modal (micrometric) analysis can only rarely be converted to an adequate chemical analysis; on the other hand it provides, with a minimum of time and equipment, quantitative information of relatively high precision on the major mineral phases. In all rocks where it can be used its advantages as an adjunct to chemical analysis should not be ignored. This is especially so in view of the current tests on chemical precision and accuracy and the serious problem of interpreting a *single* analysis of a given rock.

* Although data on TiO₂ have not been included in this previous work, determinations are practicable and have been carried out in the Cabot Laboratory at Massachusetts Institute of Technology.

Table 4. *Contributing Laboratories and Analysts*

<i>Country</i>	<i>Laboratory</i>	<i>Analyst</i>
Australia	Government Chemical Laboratory, Perth	GRACE, INGLIS
	Government Chemical Laboratory, Brisbane	WATKINS
	Mines Department, Melbourne	FIELD
	Mines Department, Sydney	REIDY
	Mines Department, Hobart	MANSON
	University of Melbourne	AMPT
Canada	Geological Survey, Ottawa	FABRY
	Department of Mines, Toronto	MODDLE
	Department of Mines, Quebec	BOILEAU, TOUSIGNANT
Finland	Geological Survey, Helsinki	WIIK
Germany	Chemisches Laboratorium Fresenius, Wiesbaden	FRESENIUS
Japan	Scientific Research Institute, Tokyo	IKAWA
	Faculty of Culture, University of Tokyo	NAGASHIMA
	Kimura Laboratory, University of Tokyo	ASARI
	Tokyo University of Education, Koishikawa	HAMAGUCHI
	Laboratory of Analytical Chemistry, University of Tokyo	KATSURA
	Asahi Glass Company Research Laboratory, Yokohama	Konoshi
	Chemical Institute, Kyushu University, Fukuoka	ISHIMORI
	Government Chemical Industrial Research Institute, Tokyo	NAKAI
	Geological Survey, Kawasaki	HIRATSUKA
New Zealand	Dominion Laboratory, Wellington	SEELYE
South Africa	Division of Chemical Services, Pretoria	VAN DER WALT
Sweden	Stockholm	SAHLBOM
Switzerland	Technische Hochschule, Zürich	JAKOB
	Universität, Bern	HÜGI

Table 4 (continued)

Country	Laboratory	Analyst
United Kingdom	Department of Mineralogy and Petrology, Cambridge University	SCOON
	Department of Geology, Leeds University	LUND, VON KNÖRRING
	Department of Mineralogy, Museum of Natural History, South Kensington	HEY
	Geological Survey, London	WATERS
	Geochemical Laboratories, Wembley	CLARKE, MILNER
	Chemical and Metallurgical Laboratories, Glasgow	HERDSMAN
United States	Geological Survey, Washington, D.C.	BRANNOCK, CARRON, FAHEY, MILTON, SHAPIRO, VLISIDIS, WARSHAW
	Geological Survey, Denver, Colorado	PECK
	Rock Analysis Laboratory, Univ. of Minnesota	OSLUND, PECK
	Department of Mineralogy, Harvard University	GONYER
	Ledoux and Company, New York	BOWDEN
	Norton Company, Worcester, Mass.	LAMAR

CONCLUDING REMARKS

This newly acquired information on precision and accuracy of silicate analysis should mark a turning point for both analysts and geologists. With the averages provided by the standard rocks, the analyst can now ascertain his range of error for each constituent, using conventional, photometric, or spectrographic methods, and, depending on the problem, select the one most suitable. The geologist should be aware of the magnitude of the experimental error peculiar to a given analyst or laboratory and direct the analysis in terms of the range of error which his problem will tolerate. In other words, an era of closer and more intelligent liaison is now indicated and indeed is imperative.

Evaluation of older analyses remains a particularly difficult task. No reliable standards can be applied to them and, as it is unlikely that the current state of silicate analysis is any worse than that of 50 years ago (it is probably much better), it seems likely that many unwarranted geological conclusions have been drawn from inadequate chemical data. This is especially so if, as is usually the case, analyses from *different* laboratories have been used for correlation work. It should therefore not occasion any surprise if chemical re-study of many suites of rocks

fails to confirm earlier findings in all respects. There has been a tendency too often to assign the lion's share of assumed error to sampling variation; appreciation and evaluation of analytical error now makes possible a fairer division of these quite different sources of variation.

Finally, it is most assuredly not the object of this paper to imply that, with these data, the last word has been said on matters of analytical precision and accuracy. If a few sparks of self-criticism are ignited in the minds of all concerned and if discussion and new projects are launched as a result, the writer and his many collaborators will feel amply rewarded.

Acknowledgments—This paper is the work of many persons, each indispensable to the overall result. As it summarizes much of the contents of two previous publications (FAIRBAIRN *et al.*, 1951; FAIRBAIRN and SCHAIRER, 1952) my indebtedness to co-authors AHRENS, DENNEN, STEVENS, SCHLECHT, CHAYES and SCHAIRER is evident. The financial aid of the Office of Naval Research is again gratefully acknowledged. Special mention of the interest and active assistance of L. H. ADAMS (Geophysical Laboratory, Washington) and of MICHAEL FLEISCHER (U.S. Geological Survey) is also in order. Finally, to the many analysts, without whose help the investigation could not have been attempted, goes a special word of appreciation for their co-operation in a difficult but not unproductive enterprise.

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The geochemistry and mineralogy of rock weathering

(1) The Lizard area, Cornwall

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ABSTRACT

The Cornish rocks (i) adamellite, (ii) granodiorite-gneiss, (iii) gabbro, (iv) hornblende-schist and (v) serpentine are described together with their weathering products. The minerals illite and kaolin are present in all the (2μ) clays derived from the rocks by weathering but chlorite and vermiculite are less widespread and talc and montmorillonoid occur in one clay only. Both mineralogically and chemically the compositions of the clays are nearer each other than are those of the rocks. The role of the minor elements in the rocks, minerals and clays in relation to the fate of the major elements is discussed.

INTRODUCTION

Both geochemistry and clay mineralogy are twentieth century sciences and owe much of their present status to the development of two single analytical methods. On the one hand, the recognition of the use of the spectrograph for the semi-quantitative determination of numerous elements gave scope to search for the rare (and often chemically similar) elements, and on the other hand, the realisation of the use of x-ray diffraction gave rise to the discovery and classification of the unique minerals found in clay. These two partly-standardised techniques have been extensively employed in the present study of element distribution in, and mineral constitution of, several igneous and metamorphic rocks and their residual weathering products.

Many English soils overlie glacial drift deposits and residual soils derived from pre-Pleistocene formations are confined to areas in the south beyond the limits of the Quaternary ice sheets. In these regions the characters of the soils strongly reflect the underlying rock type differences and a comparison of the geological map with the land utilisation map for Devon and Cornwall shows striking boundary similarities, and the diversity of rock types in the Lizard area offers a unique opportunity for studying the geochemical and mineralogical aspects of soil formation.

The Peninsula represents an uplifted wave-cut platform of Pliocene age and is flat over most of its area, rising gently from 250 ft above O.D. in the south to 350 ft a few miles further north. Serpentine forms the bulk of the country rock in the south and gabbro and hornblende-schist predominate in the east. Small outcrops of "granite"-gneiss appear enclosed by serpentine but the main mass of acid rock occurs north of the Peninsula proper in the form of the Carnmenellis intrusion. Superficial deposits, including the supposedly Pliocene beds on Crousa Down and the undated head deposits, are fairly widespread and overlie much of the serpentine and fresh gabbro. Only samples of the weathered crust immediately above the parent rock (where the risk of contamination by superficial deposits is minimised) are studied here, the rock types and their weathering products being discussed in the order adamellite, "granite"-gneiss, hornblende-gabbro, hornblende-schist and tremolite-serpentine.

Experimental methods

1. Preparation of samples

Clay ($<2\mu$ diameter) and silt (2–20 μ diameter) were separated from a suspension of the weathered rock in dilute NH_4OH by the method of PIPER (1944); the residue of sand was dry-sieved into convenient fractions.

2. Estimation of clay minerals

Prior to x-ray analysis free iron oxides were removed from the clay by saturating 0.1 gm with NH_4^+ , washing and treating with 25 ml of a solution 1.4 molar in $(\text{COONH}_4)_2\cdot\text{H}_2\text{O}$ and 0.4 molar in $(\text{COOH})_2\cdot 2\text{H}_2\text{O}$. A strip of zinc gauze was added and the mixture kept at 50–60°C for half an hour. The yellow solution containing the removed iron was decanted after centrifuging and the clay washed in the buffer solution gradually diluted to pure water.

Using a 9-cm diameter camera, the following clay specimens were photographed with $\text{CuK}\alpha$ radiation: (i) the clay flake (NAGELSCHMIDT, 1941), (ii) the glycerol-saturated clay flake (MACEWAN, 1944), (iii) the clay flake after heat treatment for several hours at 550°C, (iv) the clay powder. Semi-quantitative estimates of the different minerals in the clay, using the data contained in "X-ray Identification and Structures of Clay Minerals,"* were based on visual estimates of the intensities of the diffraction lines; values are thus approximate.

3. Analytical procedure

The methods of GROVES (1936) were used for assay of major components in the rocks, minerals, silts and clays. Minor elements were estimated by a spectrographic method using the quartz optics of a Hilger No. 478 spectrograph. Specimens were finely ground (clays and silts heated first to 350°C), mixed with carbon and loaded into carbon anodes having dimensions 3 mm diam. (int.), 5 mm deep and 4.5 mm diam. (ext.) and containing approx. 45 mg. (a) Elements Ag, Be, Co, Cr, Cu, Ga, La, Mn, Mo, Ni, Pb, Sn, V, Yt and Zr. A pointed carbon cathode was used to give an electrode gap of 10 mm and the middle two-fifths of the arc column was focused on the collimator lens; a step sector of ratio 2 : 1 was rotated in front of the slit and the spectrogram recorded for the complete burning time of 3–4 mins (8 amps) in the range 4500 Å–2800 Å on Kodak B.10 plates. (b) Elements Ba, Cs, Li, Rb and Sr. Similar to method (a) but the electrode gap was 16 mm, the step sector had the ratio 1.5 : 1 and the spectrograms were recorded in the range 9000 Å–6000 Å on Kodak IIN plates and 6000 Å–5500 Å on Kodak IIF plates. The intensities of the following lines from spectrograms of the samples were estimated visually and compared with those from spectrograms of standard mixtures: Ag 3280 Å, Ba 4934 Å, Be 3130 Å, Co 3453 Å, Cr 4254 Å, Cs 8521 Å, Cu 3274 Å, Ga 2943 Å, Li 6707 Å, La 4333 Å, Mn 4033 Å, Mo 3170 Å, Ni 3413 Å, Pb 2833 Å, Rb 7800 Å, Sn 2840 Å, Sr 3464 Å, and 4607 Å, V 3185 Å, Yt 3327 Å, Zr 3438 Å. Standard mixtures were prepared by mixing the oxides or carbonates of the elements in a sintered base consisting of SiO_2 58.5%, Al_2O_3 14%, Fe_2O_3 6.5%, MgO 4%, CaO 6.5%, TiO_2 1.0%, KCl 3.5%, NaCl 6.0%. ("Specpure" ingredients except SiO_2 .)

The standard deviations of results (duplicate spectrograms) are up to $\pm 50\%$ for Cs, Li and Rb and up to $\pm 40\%$ for the other elements. Due to the difference between the composition of the base and that of the samples (especially the minerals) the values quoted are of varying precision; the remarks of MITCHELL (WAGER and MITCHELL 1951, p. 137) are applicable. (c) Boron was determined by the method of LANDERGREN (1945); standard deviations are below $\pm 10\%$. (d) Elements Ga, In and Tl; the sensitive method of AHRENS (1945) was modified, the lines Ga 4215 Å, In 4511 Å and Tl 3775 Å used and the intensities visually estimated and compared with one-tenth their weight CaCO_3 , mixed with carbon and arced as in (a) but only the first 30 secs of the burn was recorded using Kodak P.1500 plates. The CaF band at 5291 Å was used for detection and the standards contained fluorine as CaF_2 ; standard deviations are up to $\pm 50\%$.

ADAMELLITE

1. Description of the rock

The Carnmenellis granite mass has been described by GHOSH (1934) and the parent material selected from the Bosahan quarry (Grid reference 732305) is mineralogically similar to the medium-fine grained rock he called type 2. The principal minerals are quartz (30–35%), oligoclase (20–25%), orthoclase (15–20%), muscovite (8–12%) and biotite (5–7%) and the rock may thus be described as a two-mica adamellite. The plagioclase is invariably twinned on the albite law and has usually been sericitized, especially in the less acid cores; the sericite occasionally formed with its cleavage parallel to the (001) feldspar cleavage.

* X-Ray Identification and Crystal Structure of Clay Minerals; London, 1951, The Mineralogical Society.

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